SMOKE STUDY GROUP

CORESTA

GROUPE FUMEE

PAPERS PRESENTED AT THE
COMMUNICATIONS PRESENTEES AU COURS DU

SYMPOSIUM

KALLITHEA 1990

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Smoke Study Group
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of the total population.

The mechanism of the off-taste was established. Specific conditions encountered in the dryer allow dormant spores to germinate. Entering outgrowth, cells losing osmo-tolerance during elongation are lysed, explaining population reduction. During germination, dipicolinic acid (DPA), the most abundant compound of the spore, is released (2). The direct implication of DPA (pyridine-2,6-dicarboxylic acid) in the off-taste was demonstrated by producing cigarettes with DPA levels in the range of what could be released by the natural tobacco spore population.
The subjective threshold limit established was between 100 and 500 ppb.

As germination activation is the critical step in the off-taste mechanism, the objective of the present study was to evaluate an integrated system inhibiting Bacillus spore germination.

PRINCIPLE

Beside AW and heat-shock, the amino-acid L-ALA - a physiological germinant naturally present on the tobacco - plays an important role in germination activation (3). A particularity of activation by L-ALA is a competitive inhibition of the reaction by the D-isomer : D-ALA.
The mechanism of action of both alanine enantiomers on germination is not yet clearly established (4). A proteinic receptor was localized at the surface of the spore. The allosteric site is hypothetically divided into two distinct portions. L-ALA may bind to the germination portion and activate germination mechanisms. The other portion is the inhibition part of the receptor. D-isomers of alanine and analogue amino-acids show a high affinity for this inhibition portion and can bind more strongly than L-ALA to the germination region. It was observed that the binding affinity of D-ALA is thirty times higher that that of L-ALA (5). Among all the analogues, D-ALA shows the highest affinity for the receptor and the strongest type of

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D-ALA was quantified in tobacco extract against pure Bacillus pumilus spores - the predominant strain on tobacco - and evaluated on tobacco cut-filler by measuring germination yields under conditions favouring activation. Minimum germination inhibitory concentration was found around 200 ppm. Conditions favouring germination were simulated in semi-industrial trials with and without D-ALA added. The version treated with D-ALA was subjectively in line with a standard control, while subjective off-taste was detected on cigarettes prepared with untreated tobacco.

RESUME

La microflore du tabac reséché est composée presque exclusivement de bactéries à gram + appartenant au genre Bacillus. La majorité des cellules bactériennes présentes sur le tabac sont des spores dormantes.

Une corrélation a été établie entre les conditions de séchage et les cigarettes ayant un "off-taste" (faux goût) dû à une activation microbienne. La germination des spores de Bacillus et la libération d'acide dipicolinique semblent impliquées dans les mécanismes responsables d'un "off-taste".
On a démontré que la L-alanine (L-ALA), naturellement présente dans le tabac, joue un rôle prédominant dans le processus de germination. La L-ALA se fixe sur un site à la surface de la spore, activant ainsi la germination . La D-ALA, inhibiteur compétitif de la germination engendrée par la L-ALA, a une affinité pour le site de germination plus grande que celle de la forme L et peut ainsi bloquer la germination.
La D-ALA a été spécifiquement reconnue comme agent de contrôle de la population de spores de Bacillus présentes sur le tabac. Son efficacité a tout d'abord été quantifiée dans des extraits de tabac sur une culture pure de spores de B. pumilus, espèce prédominante du tabac. Son évaluation a ensuite été faite directement sur du tabac coupé, en

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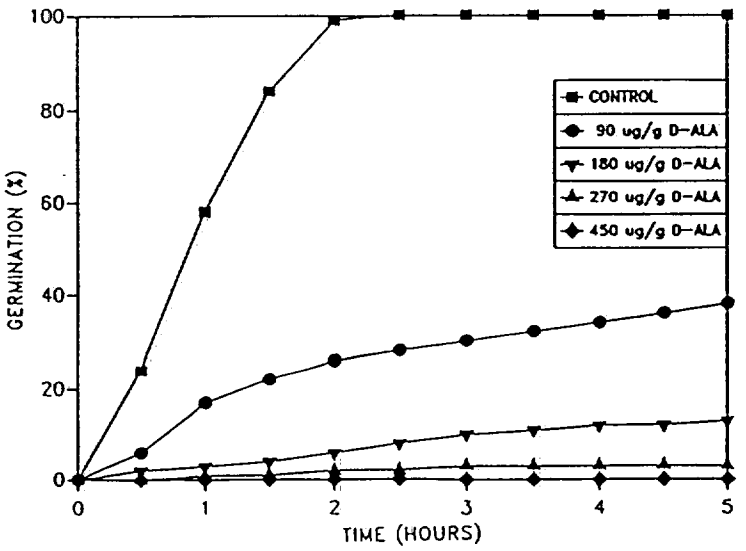
inhibition of L-ALA germination activation (6). D-ALA was evaluated as an inhibitor of Bacillus spore germination in the tobacco context.

RESULTS AND DISCUSSION

In order to avoid problems caused by the heterogeneity of tobacco microflora, a pure culture of Bacillus pumilus spores was used as a first step, to quantify the effect of D-ALA on germination. Tobacco extracts were sterilized by successive filtrations, inoculated with B. pumilus spores and incubated at 37°C. Germination was followed by the loss of absorbance at 660 nanometers. Fig. 1 shows germination kinetics for increasing dosages of D-ALA (90 to 450 micrograms per gram). In the control, germination is completed after 120 min. and then the cells start the growing process. Even with 90 ug D-ALA, the germination rate is seriously reduced. The minimal inhibitory concentration (MIC) was found to be around 200 ug/g.

FIG. 1 INHIBITION OF BACILLUS PUMILUS SPORE GERMINATION IN TOBACCO EXTRACT



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As a second step, D-ALA was tested directly on the tobacco, against its endogenous microflora, in conditions favoring Bacillus spore germination. D-ALA efficiency was evaluated

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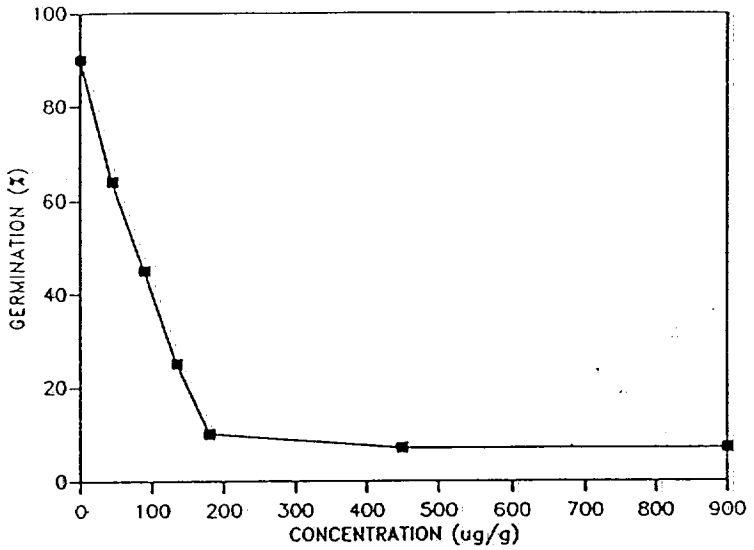
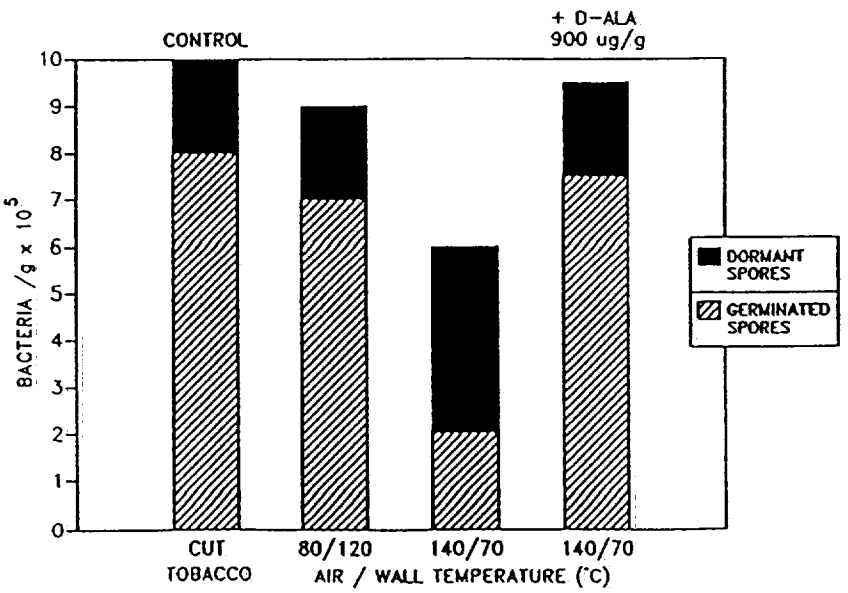
on cut-tobacco equilibrated at a AW of 0.98.
Fig. 2 presents the dose-response curve; as in tobacco extracts, the MIC is around 200 ug/g.

FIG. 2 INHIBITION OF SPORE GERMINATION BY D-ALA ON CUT TOBACCO EQUILIBRED AT AW 0.98



Finally, the effect of D-ALA in the off-taste situation was studied in pilot scale trials, by varying dryer-settings. The ratio of air temperature vs wall temperature was changed from 80°C/120°C to 140°C/70°C in the control, in order to induce spore germination and reproduce the off-taste problem (Fig. 3).

FIG. 3 SPORE GERMINATION IN CUT TOBACCO DRYER



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that conditions favoring Bacillus spore germination, such as high water activity (AW) and heat-shock, may be encountered by tobacco. The transformation of Bacillus spores into vegetatively growing cells is a sequential process involving activation, germination and outgrowth. Activation is a trigger reaction conditioning spores to germinate.

On tobacco, the key factor for microbiological activity is water activity. Bacillus vegetative growth is only possible for AW above 0.95 (1). As AW never exceeds 0.8 at equilibrium during tobacco processing, the only risk of spoilage is limited to molds. Molds can develop on tobacco surface if its AW is maintained above 0.7 for several days. However, if no Bacillus growth is expected, conditions for spore germination - e.g., heat-shock and locally high AW at the tobacco surface - could be met for a short period in the process. Such conditions could be encountered in tobacco dryers where tobacco is heated in a saturated atmosphere.

CASE STUDY

The situation was illustrated by a cigarette off-taste problem detected after the cut-tobacco drying system was modified in a factory. Tobacco coming from cutters at a AW of 0.75 was divided into two dryers operating with different settings. The subjective evaluation of cigarettes made with tobacco from each dryer showed that one dryer was producing off-taste tobacco. It was established that the off-taste situation was caused by an excessive air temperature in the dryer.

Microbiological analyses revealed a significant difference between tobacco samples taken after each dryer. In the control situation, the total bacterial count was 9×10^5 with 85% of dormant spores, while in the off-taste conditions, the total population was reduced to 4.5×10^5 and the dormant spores to 30%. After that case, similar situations were analysed with the same microbiological profile, i.e., germination of dormant spores and reduction

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mesurant le taux de germination dans des conditions favorisant une activation. La concentration minimale inhibant la germination fut estimée à environ 200 ppm. Des conditions favorisant la germination ont été simulées dans des essais semi-industriels en présence et en l'absence de D-ALA. Un "off-taste" subjectif fut détecté dans des cigarettes préparées avec du tabac non traité, alors que la version traitée avec de la D-ALA a été jugée en accord avec le standard utilisé comme contrôle.

TOBACCO MICROBIOLOGY

The microbial content of tobacco varies between one thousand and ten million organisms per gram, depending on tobacco type and origin. Three kinds of microorganisms can be isolated from tobacco : yeasts, molds and bacteria. Due to successive heat treatments in processing and low water activity, yeasts are rarely found and only a few molds can survive. The quasi-totality of the mold strains isolated and identified are characteristic members of the flora of the storage room : mainly Aspergillus and Penicillium. The only organisms that can easily survive the dessication process and heat treatments are the gram-positive spore formers Bacillus.

The microbial population of tobacco belongs exclusively (99.99%) to the Bacillus genus. Bacillus pumilus is the predominant strain found on tobacco. Bacillus subtilis and licheniformis are generally present at a few percent level as well as, sporadically, some other Bacillus stains.

A particularity of Bacillus is their ability to form spores considerably resistant to harsh environmental factors such as heat, dessication, toxic chemicals and a lack of nutrients over a long period of time.

The Bacillus life cycle involves sporulation, dormancy, spore germination, outgrowth and vegetative growth.

On tobacco, 80 to 100% of the Bacillus are present in the dormant form, the rest being germinated spores. During tobacco processing, a slight germination in the dormant spore population is naturally observed. This prefigures

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Fig.6 ACT TRIPLE : DIFFERENT ADSORBENTS

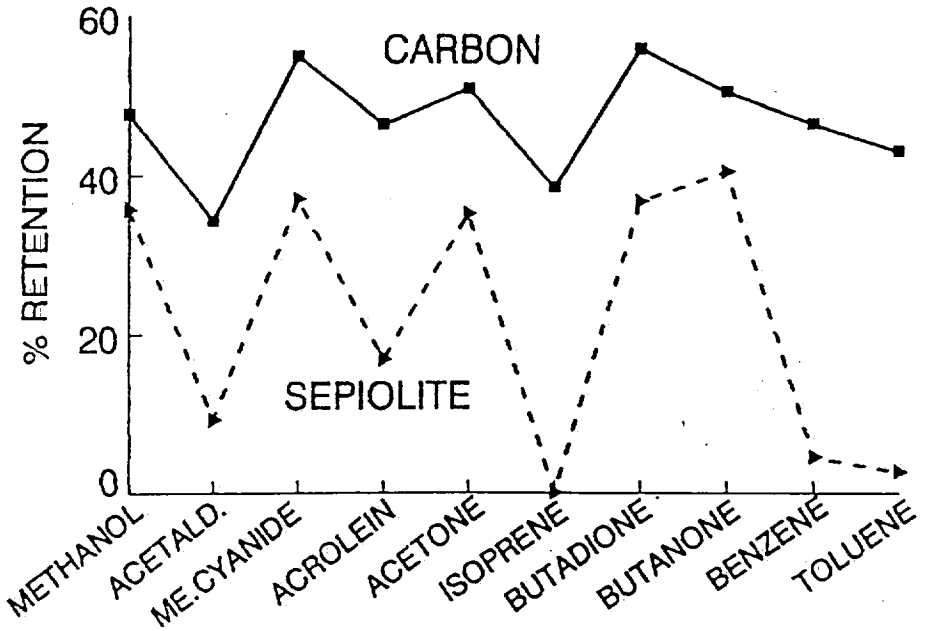
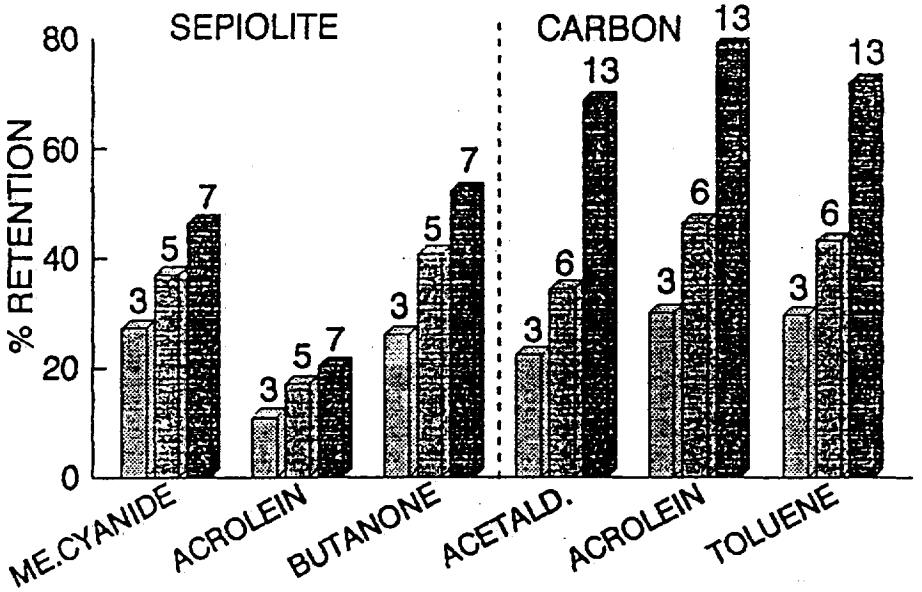


Fig. 7 ACT TRIPLE : LOADING EFFECTS



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The Adsorbent Coated Thread (ACT) Filter

The ACT filter is an entirely new method of presenting granular additives to smoke in a cigarette filter. Depending upon additive loading, a number of threads, coated with carbon and/or other granules are formed into a wrapped filter rod or placed in the axis of an acetate filter. This becomes the inner segment of a dual filter or the centre segment of a triple solid filter as shown in **Figure (5)**. In the triple solid form the carbon is fully encapsulated so that no part containing the additive is cut through during cigarette assembly eliminating loose granules in product or equipment. In use the smoke will pass through the lower pressure drop granular core, thus promoting effective exposure to the active material. Very high loading of active materials can be achieved, up to 15mg/mm depending upon the type and density of the adsorbent used. The ACT filters were tested in the same way as the AMW filters, however, in this case triple solid filters were tested using two 6mm NWA end segments with a 15mm segment of ACT filter in the centre. **Figure (6)** shows retentions for a number of organic vapour phase components at filter loadings of 5.2mg/mm (sepiolite) and 6.1mg/mm (carbon). That, is total loadings of 78mg sepiolite and 91.5mg carbon. The difference between the two adsorbents is fairly obvious with the polar sepiolite showing selective action towards polar compounds. The carbon loaded filter gives very similar behaviour to that seen previously for the AMW filter. **Figure (7)** shows the increase in component retention for a few selected compounds with increasing adsorbent levels. Again the increases shown are fairly typical of all the compounds measured at least for carbon. With the highest carbon loaded ACT filter approximately 75% of all vapour phase compounds are removed even using an unventilated cigarette.

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CONCLUSIONS

1. During the first 6 to 8 weeks, tobacco column menthol content is dependent upon the original site of application and will increase or decrease accordingly. It then slowly (but steadily) decreases. Filter tip menthol content behaves in a similar but opposite fashion.

2. Within certain limits, the stabilized menthol content of the filter is independent of the original site of application.

3. During the stabilization period (first 2 to 3 weeks), menthol delivery is dependent upon application site. After stabilization, all cigarettes deliver approximately equivalent amounts of menthol, which slowly decreases with time.

4. During the stabilization period, applying some menthol to the filter (between 25% and 50%) minimizes changes in menthol delivery with time.

5. After stabilization, the net gain in the menthol content of the filter tips after smoking is small (<.3mg) and constant.

6. After stabilization, menthol utilization decreases over time at a relatively constant rate and is independent of the original application site.

7. A significant amount of menthol elutes from the filter when smoke passes through the filter. This is more than offset by the quantity of menthol in the particulate matter trapped by the filter.

8. Menthol delivery due to the tobacco smoke is apparently independent of the menthol content of the filter tip.

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BIOCONTROL OF TOBACCO MICROFLORA BY D-ALANINE

BIOCONTROLE DE LA MICROFLORE DU TABAC PAR LA D-ALANINE

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SUMMARY

The microbiological make-up of redried tobacco is almost exclusively made of bacteria from gram-positive Bacillus genus. On tobacco, most of the Bacillus cells are present in a dormant spore form.

A correlation was established between tobacco-dryer conditions and cigarette off-taste caused by microbial activation. Germination of dormant Bacillus spores and the subsequent release of dipicolinic acid seem to be involved in the mechanism resulting in the off-taste.

The transformation of Bacillus spores into vegetatively growing cells is a sequential process involving activation, germination and outgrowth. The key is the activation step which is a trigger reaction that conditions spores to germinate. It has been shown that the amino-acid L-alanine (L-ALA) naturally present in tobacco plays a predominant role in the germination process. L-ALA binds to a germination site at the surface of the spore, thus causing activation. A competitive inhibitor for the initiation of germination by L-ALA is D-alanine (D-ALA). The binding affinity of D-ALA to the germination site is stronger than that of L-ALA, so it is able to block the initiation of germination.

D-ALA was evaluated specifically as a control mechanism for the Bacillus spore population of tobacco. The efficacy of

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FIGURE 5

PRINCIPAL COMPONENT ANALYSIS OF FLUE-CURED TOBACCO

GRADES OF 1986, 1987 AND 1988 CROPS

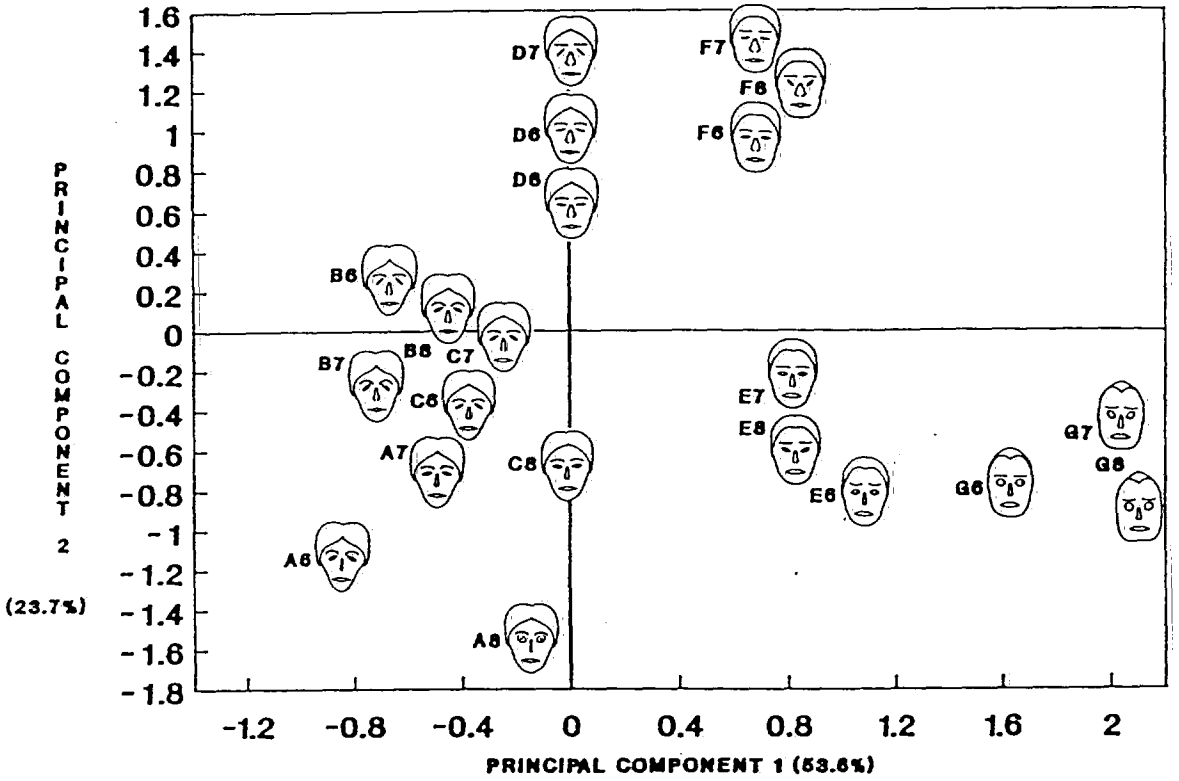
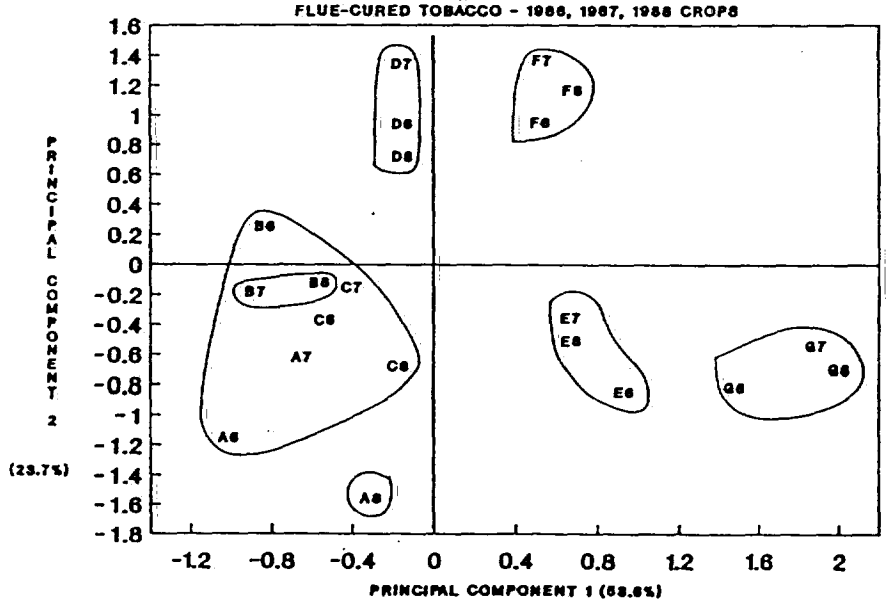


FIGURE 6

HIERARCHICAL CLUSTER ANALYSIS

(NEAREST NEIGHBOUR - EUCLIDEAN DISTANCE)

FLUE-CURED TOBACCO - 1986, 1987, 1988 CROPS



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Chlorides and Sugar-Nicotine (Sug-Nic), Nitrogen-Nicotine (Nit-Nic) ratios. The chemical analyses were carried out according to CORESTA, ISO and other standard methods used for tobacco.

c. Data Analysis

The following computer software were utilized for the statistical analysis of the information: Systat 4.1, Statgraphics 4.0, Minitab 6.1, Lotus 2.2, Asym, and Harvard Graphics 2.13.

RESULTS AND DISCUSSION

a. Evaluation of Tobacco Grading Systems

This evaluation was made using discriminant analysis applied to seven grades of the 1988 Flue-cured tobacco crop. A preliminary variance analysis showed that the nine chemical parameters considered had a discriminant capability. The criteria for the classification were Mahalanobis' minimum distances (D^2_{iz}), according to the following definition:

Classify Z into πi, if:
$D^2_{iz} = \min \{D^2_{1z}, D^2_{2z}, ..., D^2_{kz}\}$; where i = 1,.,.,., 7, z = 1, .,.,., 62

The results are shown in Table 3, where the "total" row represent the number of pre-classified samples in each group according to conventional criteria, and the columns contain the number of samples classified by the discriminant analysis. Grade A is taken as an example: eight out of nine samples were classified as A and one was re-classified as C. Four samples of the 62 analyzed were re-classified in different grades, indicating that the discriminant analysis reproduced the conventional grading at 93.5%.

Table 3. Discriminant Analysis (DA)
1988 Crop. Nine Variables by Grade

Grade	Discriminant Analysis						
	A	B	C	D	E	F	G
A	8		1				
B		8		1			
C	1		8		1		
D				8			
E					8		
F						9	
G							9
Total	9	8	9	9	9	9	9
Classified by DA	8	8	8	8	8	9	9
Misclassified	1	0	1	1	1	0	0
Reproduced (%)	89	100	89	89	89	100	100

Table 4. Principal Component
Analysis (PC). Component Loadings

Variable	PC1	PC2	PC3
Sugar	-0.96	0.14	-0.03
Nitrogen	0.83	0.08	0.53
Nicotine	0.14	0.98	0.05
PEE	0.60	0.18	-0.69
TVB	0.87	0.26	0.26
Ashes	0.65	-0.46	-0.51
Chlorides	0.45	-0.14	-0.26
Sug-Nic	-0.90	-0.35	0.01
Nit-Nic	0.47	-0.78	0.37
Variance (%)	48.95	22.73	14.35
Variance Accumulate (%)	48.95	71.68	86.03

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Fig.4 AMW DUAL FILTER : EFFECT OF CARBON LOADING

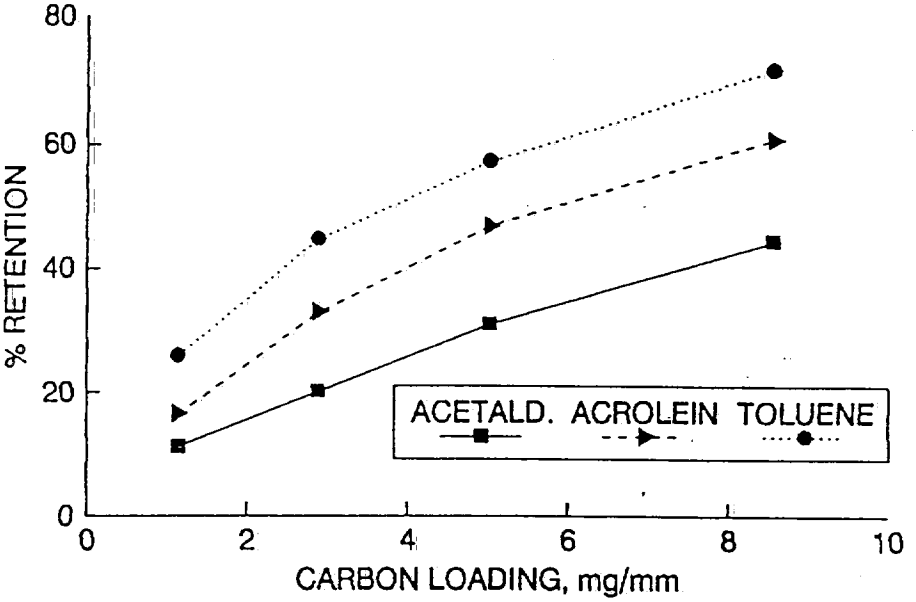
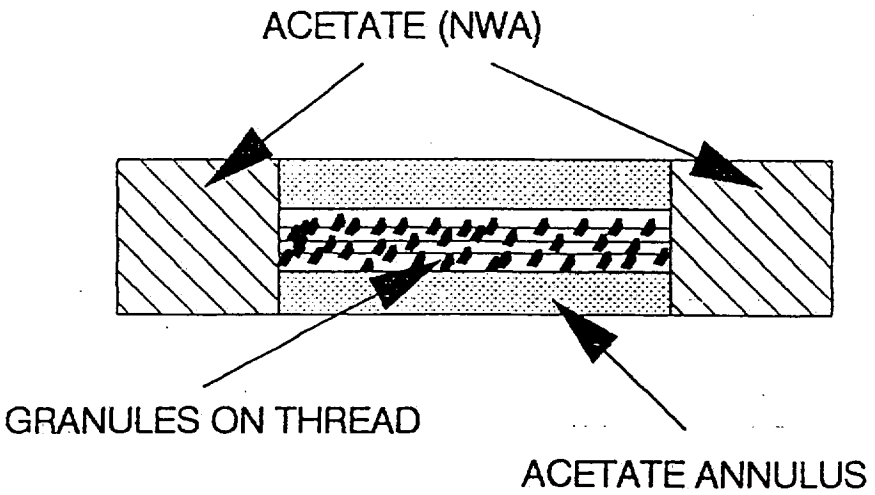


Fig. 5 ACT TRIPLE SOLID FILTER



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Tobacco treated with 900 ug/g D-ALA was evaluated in the same conditions. This time, the total number of bacteria as well as the spore proportion remained constant at the level of the cut-tobacco values. The subjective evaluation of the finished products showed a clear correlation between microbiological status and cigarette taste (Table 1).

TABLE 1
SUBJECTIVE EVALUATION OF CIGARETTES

VERSION	AIR / WALL TEMPERATURES	COMMENTS
CONTROL	80 / 120	Standard quality
TRIAL	140 / 70	Off-taste bitter, acidic
TRIAL + D-ALA	140 / 70	Standard quality

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Figure 5
Menthol Utilization:
Percent Delivery of Applied

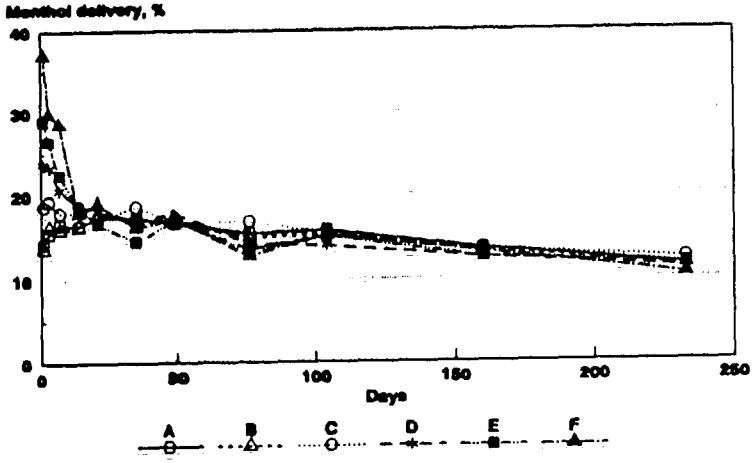


Figure 6
MENTHOL DELIVERY

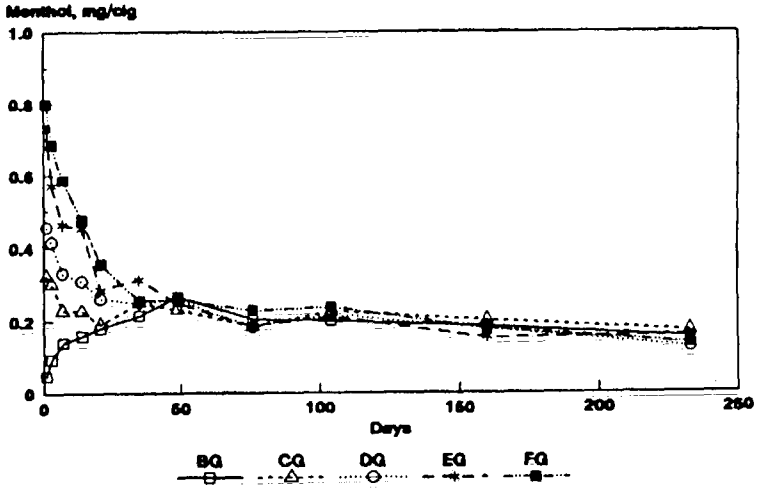


Figure 7
MENTHOL DELIVERY

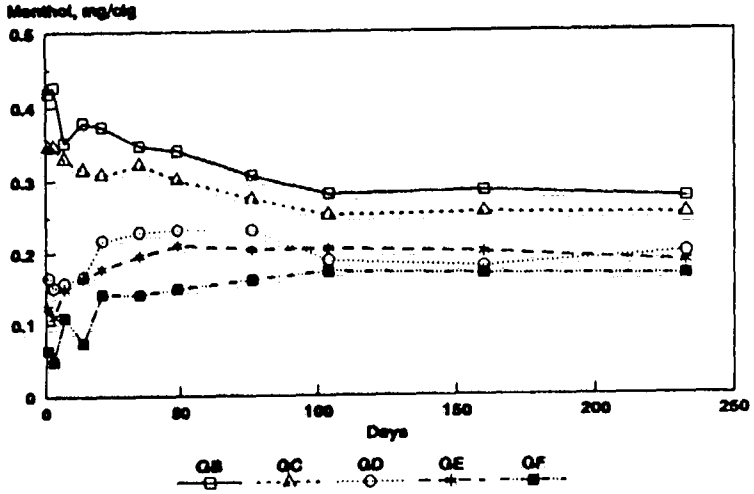
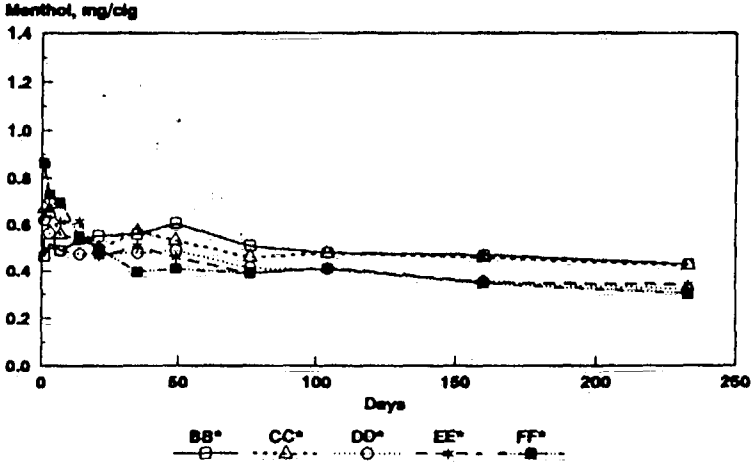


Figure 8
RECONSTITUTED MENTHOL DELIVERY
TIP DELIVERY PLUS COLUMN DELIVERY



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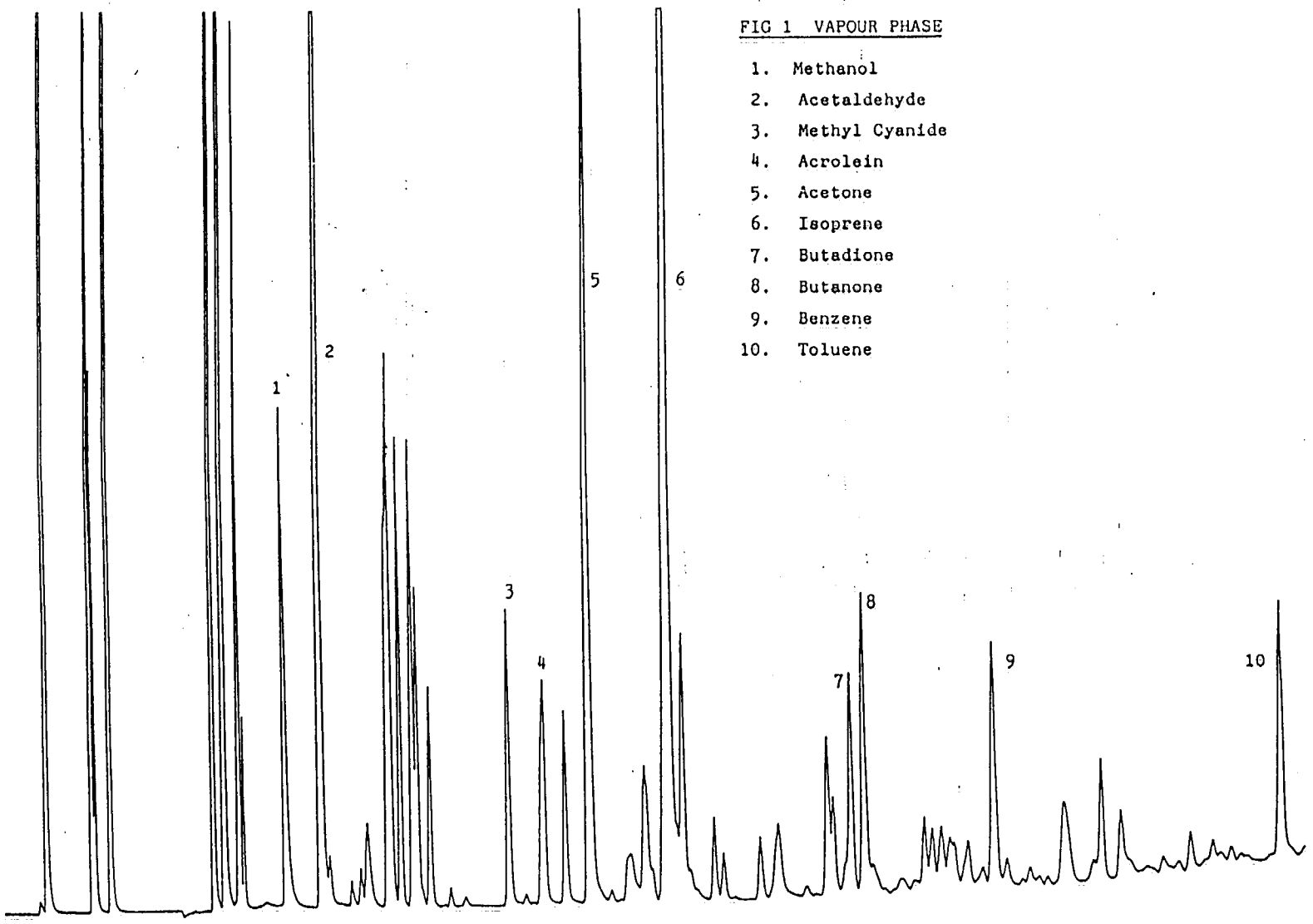

FIG 1 VAPOUR PHASE

1. Methanol
2. Acetaldehyde
3. Methyl Cyanide
4. Acrolein
5. Acetone
6. Isoprene
7. Butadione
8. Butanone
9. Benzene
10. Toluene

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INTRODUCTION

The multivariate analysis is a statistical technique for data analysis that allows to work simultaneously with several variables, giving the possibility of an integral analysis of the information. Among the statistical techniques of this type, we can mention the Discriminant Analysis, the Principal Component Analysis (PC) and the Cluster Analysis.

The discriminant analysis is a supervised technique that starts from classified observations to determine whether or not an object belongs to an assigned population. The objective of the principal component analysis is to reduce the original variables to a few components without a significant loss of information.

The cluster analysis is a non-supervised classification technique which allows to group the objects according to some similarity criterion.

In this study, the foregoing techniques were applied for analysis of the tobacco grading system, the comparison between crops and the definition of equivalences between different grades of tobacco. A non-hierarchical cluster analysis was carried out with samples of different varieties so as to gather sample groups having similar chemical characteristics.

EXPERIMENTAL

a. Sample Identification

For the evaluation of the grading system, seven grades of the 1988 Flue-cured tobacco crop were classified according to conventional criteria (color, body, size, stalk position, etc.). The comparison of crops was made between 1986, 1987 and 1988 Flue-cured tobacco crops (Table 1). To group tobacco samples according to their chemical similarities, samples of Flue-cured, Burley, Black air-cured and another type of air-cured called Extra, were employed (Table 2).

Table 1. Sample identification. Seven Flue Cured Grades (A-G). 1986, 1987, 1988 Crops

1986	n	1987	n	1988	n	Description
A6	5	A7	9	A8	9	Cutters
B6	5	B7	8	B8	8	Leaf
C6	8	C7	9	C8	9	Lugs
D6	6	D7	9	D8	9	Smoking Leaf
E6	6	E7	9	E8	9	Primings
F6	7	F7	9	F8	9	Upper Leaf
G6	5	G7	9	G8	9	Mixed-non descript

n: number of samples analyzed

Tabla 2. Sample Identification (ID) for Non-Hierarchical Cluster Analysis

ID	n	Description
H	10	Leaf, Extra air-cured
I	10	Leaf, Black air-cured
J	10	Leaf, Flue-cured
K	9	Stem, Flue-cured
L	10	Leaf, Burley

n: number of samples analyzed

b. Chemical Quality Parameters

The parameters used as quality criteria were: Reducing Sugars, Total Nitrogen, Nicotine, Total Volatile Bases (TVB), Petroleum Ether Extracts (PEE), Ashes,

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Fig. 2 AMW DUAL FILTER

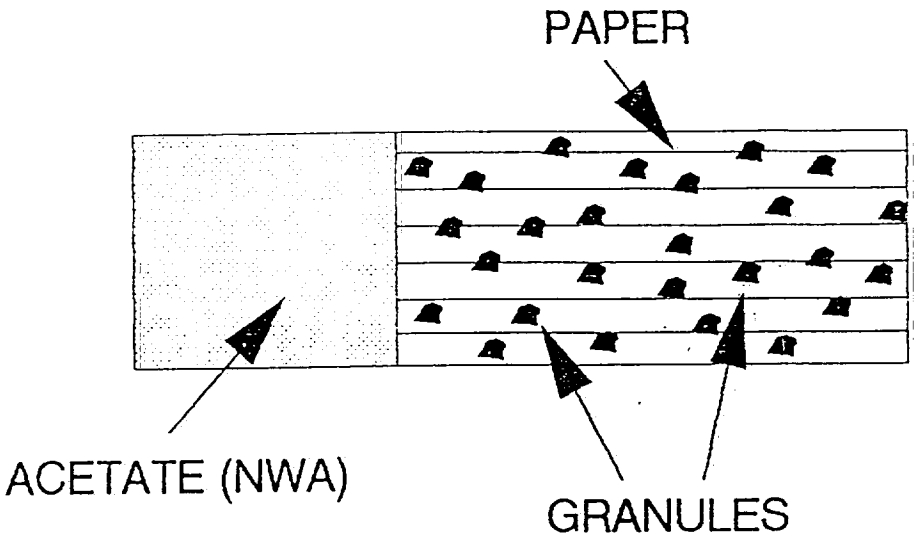
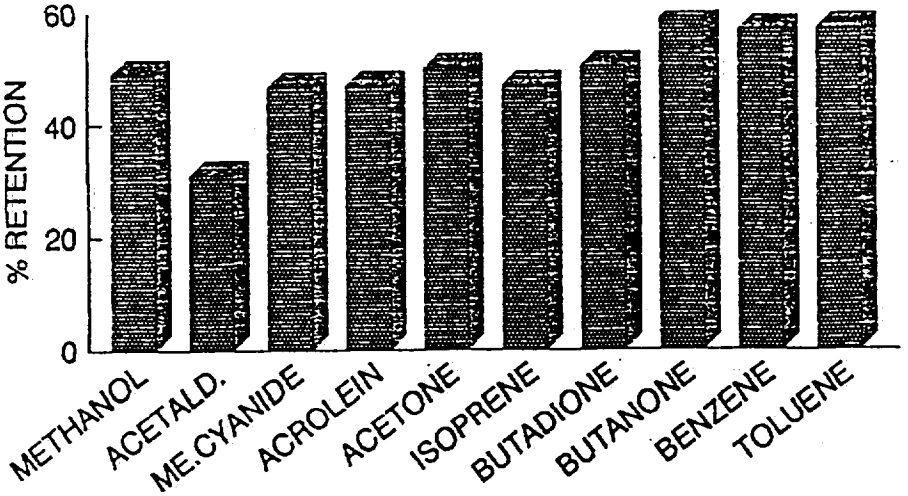


Fig. 3 AMW DUAL : V.P. RETENTIONS



(8 + 13) X 24.4 mm : CARBON 65.3 mg/FILTER

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No.	Papers/Communications	Page
S07	M. Sorak-Pokrajac, M. Dermelj, Z. Slejkovec, I. Eskinja SELENIUM CONTENTS IN TOBACCO AND MAINSTREAM CIGARETTE SMOKE	79
S08	B. S. Dattilo, S. G. Rossi ANALYSIS OF LOW MOLECULAR WEIGHT CARBOHYDRATES OF TOBACCO BY HIGH PERFORMANCE ION CHROMATOGRAPHY	87
S09	M. Dermelj, M. Sorak-Pokrajac, J. Smrke, A. R. Byrne, P. Stegnar QUANTITIES OF ARSENIC AND ANTIMONY IN TOBACCO AND SMOKING CONDENSATE	95
S10	K. D. Brunnemann, J. E. Cox, M. R. Kagan, D. Hoffmann ANALYSIS OF SELECTED ENVIRONMENTAL TOBACCO SMOKE COMPONENTS IN INDOOR AIR BY THERMAL DESORPTION-GC-MS	100
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S15	L. Tomic, S. Delac SORBITOL EFFECTS ON TAR, NICOTINE AND CARBON MONOXIDE YIELDS OF CIGARETTES	140
S16	W. Xiaochen, X. Jianping, X. Qixin SYNTHESIS OF 2-ALKYL-5-OXOHEXANOIC ACIDS AND ESTERS AND THEIR EFFECT ON CIGARETTE SMOKE	144
S17	M. Nikolic, D. Djokovic, M. Dzemidzic PHENOLS IN TOBACCO SMOKE - POSSIBLE ROUTE FOR THEIR SYNTHESIS FROM ADDED SUGARS	151

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this study only used chemical variables, the inclusion of other sensitive parameters, such as organoleptic and physical variables in addition to the chemical ones, would give a more complete information and strengthen this technique for the foregoing applications.

FIGURE 7

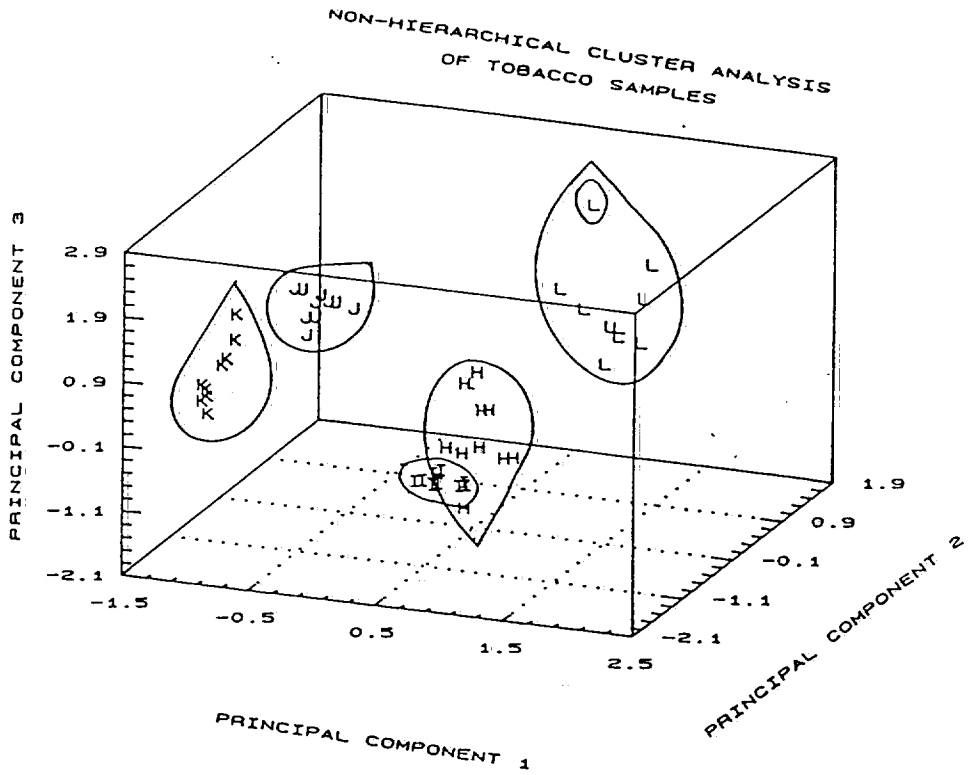

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Fig.1. Size distributions

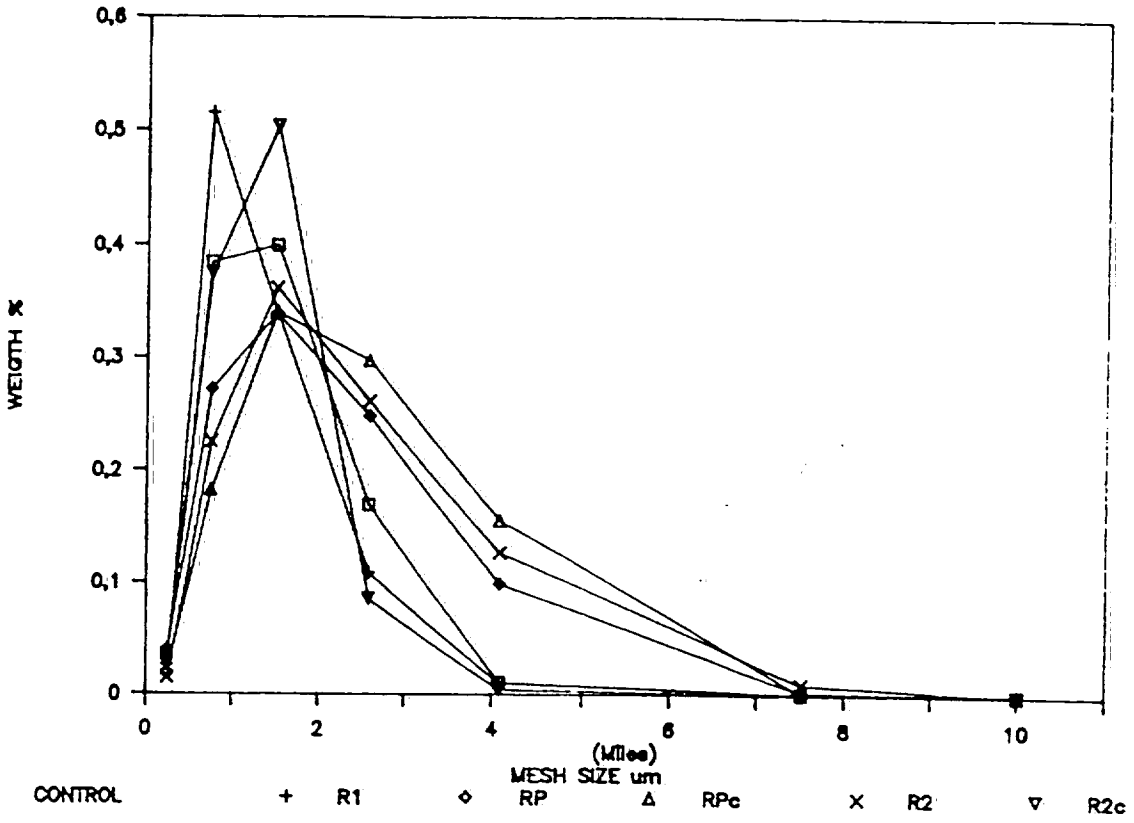

Table 2 .- Test Chi2 for the distributions

	Ctrl	R1	R2	RP	R2C	RPc
Ctrl.	--	7.72 NS	147. **	81.05**	7.38 NS	217.2**
R1		--	178.6**	108.4**	12.84**	263.5**
R2			--	5.36 NS	42.12**	5.4 NS
RP				--	32.06**	57.94**
R2c					--	58.53**

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Fig.2a.Anion distributions

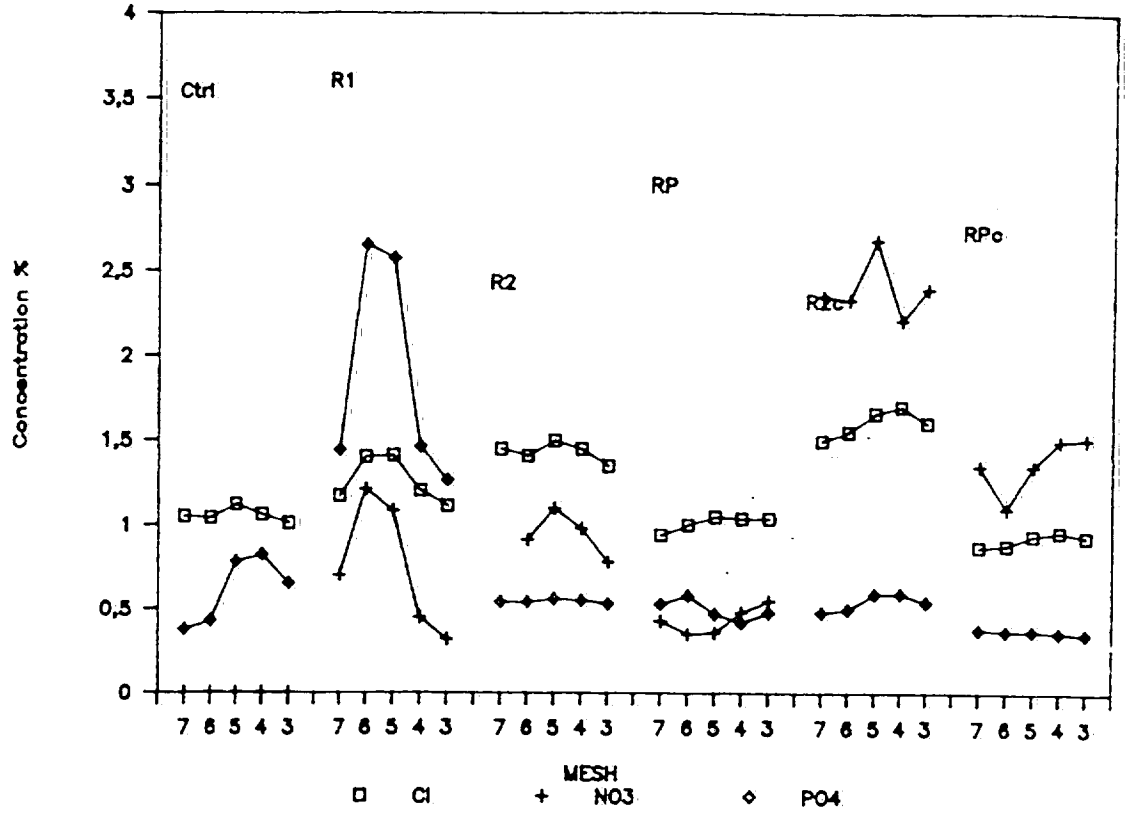
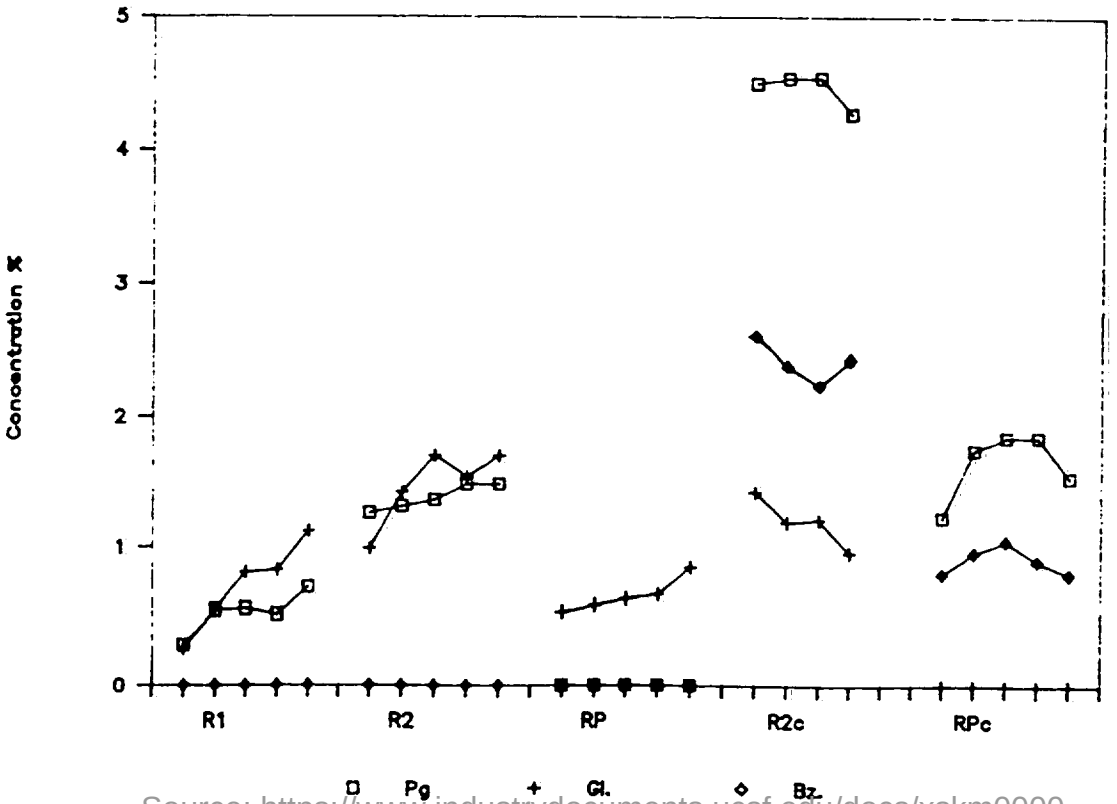


Fig.2b. Casing distributions



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Menthol content of the filter tips and tobacco columns was determined immediately after manufacture and then periodically for the next eight months. At the same time, the cigarettes were smoked to determine menthol deliveries. These results were then correlated with the original site of menthol application as a function of time. The test schedule and scheme are given in Table 2. Testing was done more frequently during the early part of the study to provide more detailed information during the steepest part of the menthol transfer curve.

All cigarettes were smoked on a Filtrona SM350 machine according to Coresta protocols, with the exception that they were not conditioned. This was done in order to simulate actual smoking conditions as well as to minimize loss of menthol to evaporation. Twenty cigarettes were smoked through four Cambridge traps.

Water, nicotine, and menthol deliveries were determined via gas chromatographic analysis of alcoholic extracts of the smoked Cambridge filters. Water was quantified on a Poropak Q column and thermal conductivity detector. Nicotine and menthol were quantified on a 30 meter J&W DB-WAX megabore column (1.0μ film thickness) and flame ionization detector. A Hewlett Packard 5880A GC was used for all analyses.

Menthol in smoked and unsmoked (blank) filter tips was determined by GC analysis of alcoholic extracts of the filter tips. Menthol content of the tobacco columns was determined by duplicate aqueous distillations of the tobacco of two cigarettes, followed by GC analysis.

DISCUSSION

The migration of menthol within a cigarette is relatively predictable. Figure 1 shows the menthol content of the filter tip as a function of time for the samples (samples A and B are replicates of the 100% menthol on tobacco variant). As expected, the cigarettes to which menthol was applied mostly to the filter show a rapid loss from the filter, whereas the cigarettes to which menthol was mostly applied to the tobacco show a rapid increase in filter menthol. A slow but steady gain in filter menthol follows this initial equilibration period; this is due to the relatively greater solubility of menthol in plasticized cellulose acetate.

Mirroring this is the decrease in menthol from the tobacco columns (Figure 2). Initially, excess menthol from the filter tip rapidly transfers to the tobacco, creating a rise in menthol content for samples E and F. There follows a slow loss of menthol for all samples, as menthol is absorbed by the filter, maintaining a chemical potential between tobacco and filter. Note that sample D (menthol applied 50/50 filter/tobacco) exhibits very little menthol migration during the equilibration period.

The separation into two distinct groups is due to the difficulty of applying significant quantities of menthol to the filter. A material balance indicates that samples D, E, and F contained approximately 2.5 mg menthol, which is 0.5 mg short of nominal. Subsequent figures have been corrected for this shortage.

Menthol delivery is shown in Figure 3. Not surprisingly, the cigarettes with large amounts of menthol applied to the filter show a very high delivery for

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Helium was used as the carrier gas at a flow rate of 2.1cm^3/min through the column, with a split ratio of 16:1. The GC analysis time was approximately 32 minutes per sample.

Data was collected using a Spectra Physics SP 4290 computing integrator. A typical chromatogram is shown in **Figure (1)**.

All results were the mean of three analyses.

RESULTS

The method has been used in the testing of two new types of carbon filter, both of which have high adsorbent loading capability.

The AMW Filter

Carbon, or other adsorbent granules, are distributed throughout an embossed paper segment. The adsorbent is held to the paper by use of a small amount of thermoplastic polymer, precoated onto the granules, and subsequently heat-treated. High loadings of adsorbent can be achieved, depending on the density: for example, up to about 9mg/mm of activated carbon. Tests were done on 21 x 24.4mm dual filters with 8mm NWA mouth end segments and 13mm AMW segments, **see Figure (2)**. The filters were assembled to tobacco rods, and tested after several weeks storage. Indirect retentions were calculated by comparison of mean values (3 x 8 cigs) with those from the tobacco rods alone.

Figure (3) shows retentions for a number of organic VP compounds at a filter loading of 5.02mg/mm, ie a total carbon loading of 65.3mg/filter. As would be expected with carbon, the retentions are fairly similar for different compounds, with a slight tendency to increase with higher boiling compounds such as butanone and toluene.

Figure (4) shows the effect of carbon loading for a few selected compounds, and the increases shown are typical of all of the compounds measured.

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MEASUREMENT OF THE PERFORMANCE OF SOME NEW VAPOUR PHASE ACTIVE FILTERS BY AN IMPROVED GAS CHROMATOGRAPHIC METHOD.

Michael Dunn, John F. Graham, Richard J.K. Shepherd and Michael J. Taylor,
Filtrona International Limited, Bedesway, Jarrow, Tyne and Wear, England.

SUMMARY

The increasing world-wide interest in the use of cigarette filters containing granular adsorbents has led to the need for a rapid method to measure the activities of such materials in cigarette filters. Previously, the vapour phase activity of filters was commonly measured by Gas Chromatography using long packed columns with the associated problems of high bleed rates and the time needed to obtain satisfactory resolutions of the majority of vapour phase compounds. An improved GC method has been developed for the rapid determination of vapour phase constituents in cigarette smoke using the high resolution now available from fused silica bonded phase capillary columns. Relatively undemanding experimental conditions are required, a temperature programme from 40 to 225°C allowing a good separation to be achieved in twenty five minutes. This method has now been in routine use at Filtrona for over two years without any deterioration in column performance.

Two new types of filters have been studied, both of which allow high loadings of granular materials to be achieved. Typical performance data of these filters is reported, showing their effect on the vapour phase of cigarette smoke. A comparison of the use of carbon and sepiolite as adsorbents is also given.

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INTRODUCTION

In recent years, there has been an increase in demand for filters containing adsorbents, particularly carbon. Such filters are now in use in many countries, e.g. Italy, Korea, China and of course in Japan. The

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TABLE 2
CONTENT OF TOTAL NITROGEN IN THE TOBACCO SAMPLES
BY WET CHEMISTRY AND NIR ANALYSES

SAMPLE	TOTAL NITROGEN BY WET CHEMISTRY %	TOTAL NITROGEN BY NIR %	RESIDUAL VALUES WET CHEM. - NIR
1	1.76	1.82	-0.06
2	2.07	2.18	-0.11
3	1.67	1.78	-0.11
4	2.39	2.24	0.15
5	2.01	1.90	0.11
6	2.44	2.35	0.09
7	2.69	2.89	-0.20
8	2.40	2.68	-0.28
9	2.09	2.17	-0.08
10	1.72	1.80	-0.08
11	2.61	2.59	0.02
12	2.48	2.33	0.15
13	2.36	2.28	0.08
14	3.01	3.05	-0.04
15	2.32	2.39	-0.07
16	1.05	0.98	0.07
17	1.01	0.97	0.04
18	1.15	1.26	-0.11

It may be concluded that the content of total alkaloids and total nitrogen in tobacco samples can be determined with sufficient accuracy by the near infrared reflectance spectroscopy. The NIR technique is fast, reproducible, non-destructive and irreplaceable when a large number of samples has to be processed in a short time with low material and power consumption. Finally our experience has shown that for each year, i.e. each season and for each type of tobacco, the calibration has to be readjusted.

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Fig.3.Basal surface vs total casing

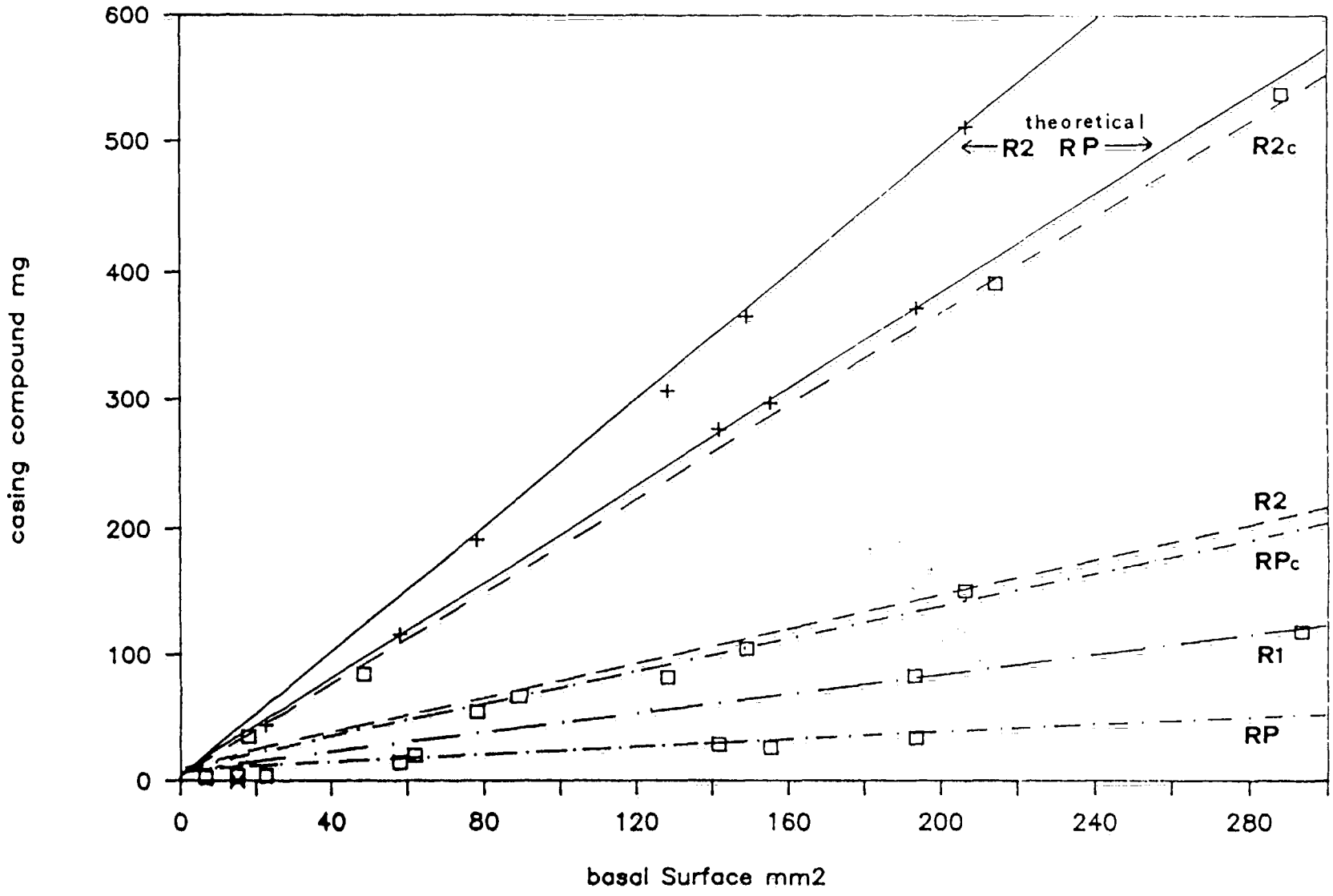

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TABLE 1

CIGARETTE PROPERTIES

Length	84 mm
Tip Length	21 mm
Tip Weight	170 mg
Tip Circumference	25.0 mm
Tip Pressure Drop	68 mm H_2O
Ventilation	None
Tobacco	Standard Domestic Blend
Plasticizer	6% (Nominal) (Triacetin)
Menthol (Target)	3 mg/cig
Deliveries	Full Flavor

TABLE 2

SAMPLE IDENTIFICATION

	TIP MENTHOL % of TOTAL	COLUMN MENTHOL % of TOTAL
A	0	100
B	0	100
C	25	75
D	50	50
E	75	25
F	100	0
G	0	0

SAMPLES TESTED

Primary - A, B, C, D, E, F, G
CASE I (Filter/Tobacco Column) - BG, CG, DG, EG, FG
CASE II (Filter/Tobacco Column) - GB, GC, GD, GE, GF

TESTING SCHEDULE

DAYS - 0, 2, 6, 13, 20, 34, 48, 76, 104, 160, 233

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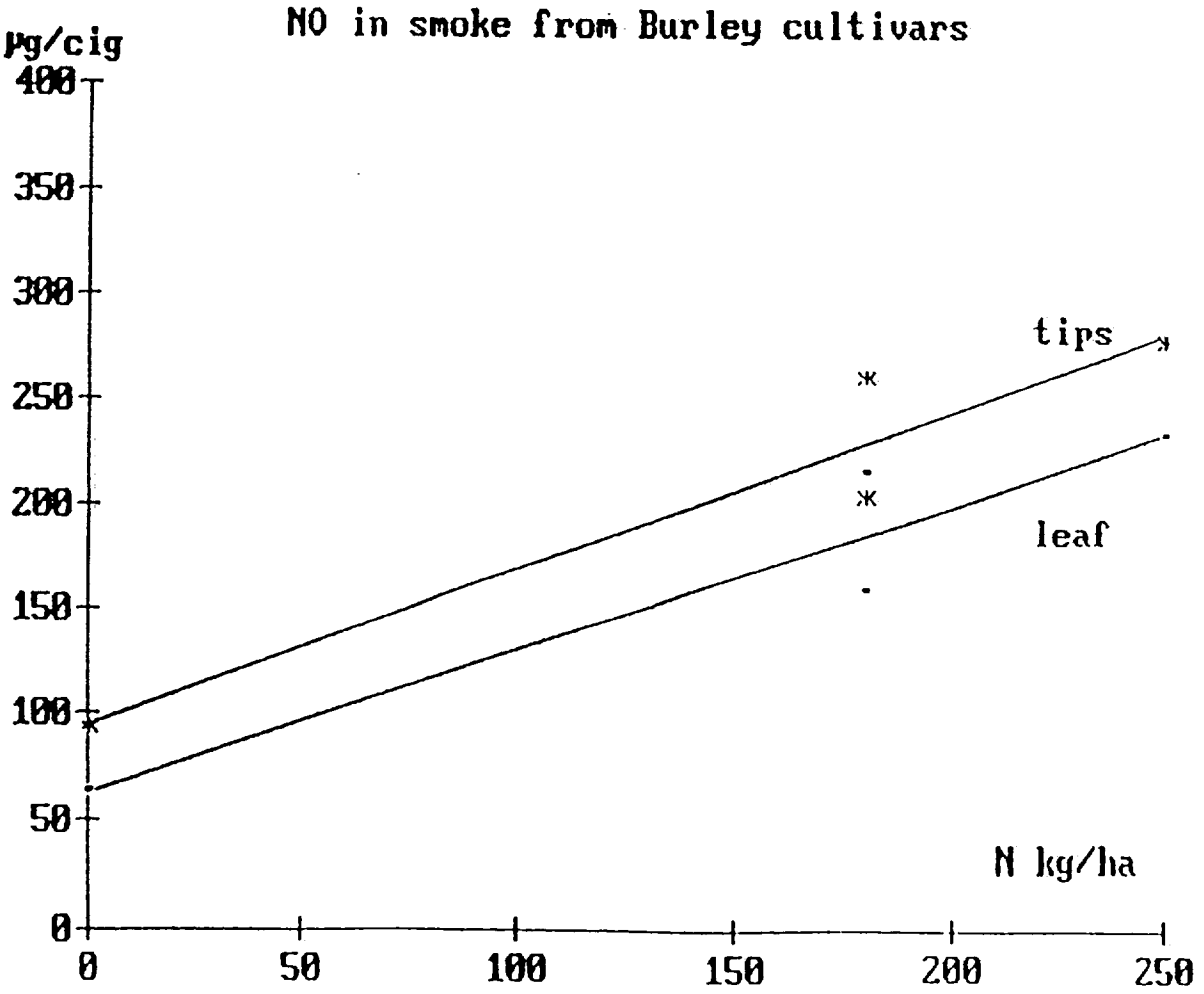
TOBACCO BREEDING AND THE TASKS IN FUTURE

An excessive N-fertilization in tobacco cultivation used for an increase in yield is creating high levels of nitric oxide in tobacco smoke. This is shown by the German cultivar Bad. Burley E in the harvesting grade "leaf" and "tips". Altogether, the Burley cultivars are very high in nitric oxide content. An unexpectedly low nitric oxide content was found in the German Geudertheimer cultivars. Independently of fertilization and harvesting grades it has been found that the nitric oxide content is significantly correlated to the differences in the tobacco cultivars. Therefore the nitric oxide content has to be taken into consideration as a quality and breeding attribute for cultivars. The other compounds in tobacco smoke tar and carbon monoxide do not differ so much and have less variability according to parameters.

Graph 1



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Five tobacco samples showed a significant discrepancy between the values obtained by wet chemistry and by spectrum analysis, amounting to 6.33% of the total number of samples tested (elimination criterion = RES/RSD ≥ 2).

In absolute values, the discrepancies amounted to up to 0.28%, and so the average error in determining the total alkaloids in the test set was +/- 6.2%. One part of the results is shown in Table 1.

The values for total nitrogen obtained in the same way are shown in Table 2, and a significant difference was observed in only 4 samples, which amounts to 5.1 % of the total number and so the scattering of the results ranged within a limit of +/- 5.5 %. Considering that in wet chemistry analysis the average error for total alkaloids ranged within a limit of 4.5 %, while the average error for total nitrogen ranged within a limit of 3 %, the results obtained by measurement of the amounts of these species by an INFRAALYZER are satisfactory, especially if the time and chemicals needed to perform analyses by wet chemistry are taken into account.

TABLE 1
CONTENT OF TOTAL ALKALOIDS IN THE TOBACCO SAMPLES
BY WET CHEMISTRY AND NIR ANALYSES

SAMPLE	TOTAL ALKALOIDS BY WET CHEMISTRY %	TOTAL ALKALOIDS BY NIR %	RESIDUAL VALUES WET CHEM. - NIR
1	3.54	3.61	-0.07
2	1.03	0.95	0.08
3	4.58	4.33	0.25
4	4.55	4.64	-0.09
5	0.61	0.57	0.04
6	0.45	0.40	0.05
7	1.74	1.66	0.08
8	2.59	2.51	0.08
9	3.27	3.31	-0.04
10	3.21	3.16	0.05
11	4.97	4.99	-0.02
12	5.03	4.88	0.15
13	5.52	5.55	-0.03
14	3.62	3.63	-0.01
15	3.51	3.53	-0.02
16	1.92	1.88	0.04
17	2.83	2.55	0.28
18	2.44	2.22	0.22

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These same samples were analyzed by the Principal Component method (PC) using the correlation matrix to avoid the effect of differences in the units of measure (Table 4). The loading vectors of the components represent the correlation between each PC and the variables analyzed. PC1 includes information about nearly 50% of the system's total variance, representing mainly the variables Reducing Sugars, Nitrogen, TVB, Ashes, Chlorides and the Sug-Nic ratio; while PC2, dominated by Nicotine and the Nit-Nic ratio, represents almost 23% of the total. Thus, the nine parameters can be reduced to three new variables (PC1, PC2, PC3) involving 86% of the information contained in the original variables, significantly reducing the dimensions of the population and allowing a comprehensive analysis of the information. The discriminant analysis shown in table 3 was reproduced at 93.6% when the three PC were used (Table 5); an analysis with four PC gave the same results as with three.

Table 5. Discriminant Analysis (DA)
1988 Crop. Three Principal Components

Grade	Discriminant Analysis						
	A	B	C	D	E	F	G
A	8		2				
B		8		1			
C	1		7		1		
D				8			
E					8	1	1
F						8	
G							8
Total	9	8	9	9	9	9	9
Classified by DA	8	8	7	8	8	8	8
Misclassified	1	0	2	1	1	1	1
Reproduced (%)	89	100	78	89	89	89	89

Using PC1 and PC2, a dispersion diagram was made for the grades considered (Fig. 1); grades F and G showed the highest variability; this fact was confirmed with the results of the generalized variance. The face system developed by Riedwyl and Flury in 1986, where each element of the face represents a different variable (Fig. 2), was used with the mean vectors of each grade in their first two PC, and also with the mean vectors of the nine original variables (Fig. 3). The differences or similarities between grades (higher or lesser distance between faces) can be observed, as well as the differences between variables in each grade (differences in face's elements).

b. Comparison of Crops

Seven grades from each of the 1986, 1987 and 1988 Flue-cured crops were compared among them by means of their PC. Figure 4 shows how the grades D, E, F, G form separate groups, indicating a good correlation within a group for different crops. Grades B and C are quite near and grade A had the highest

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QUANTITATIVE CHANGES IN VOLATILE AND NON-VOLATILE CARBONYLS OF DIXIE SHADE WRAPPER TOBACCO FROM HARVESTING TO AGEING

Abstract

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Quantitative changes in carbonyls of cigar wrapper tobacco (CV. Dixie Shade) were studied during 50-days of air-curing, 90-days of fermentation and 1 year of ageing of leaf. Volatile, non-volatile and total carbonyls increased enormously during the yellowing stage of air-curing, but thereafter declined gradually. An overall increase of 18, 37 and 30 per cent of their initial contents was observed in the volatile, non-volatile and total carbonyls, respectively during the whole process of air-curing. Non-volatile carbonyls increased during the later stages of fermentation, whereas more than half of the volatile carbonyls were lost during early fermentation due to their highly volatile nature. During storage, both volatile and non-volatile carbonyls were lost to the extent of about half of the volatile carbonyls and one-fourth of the non-volatile carbonyls. At the end of ageing, ascending stalk positions contained higher amount of non-volatile carbonyls as compared to the leaves of descending stalk positions, whereas volatile carbonyls were not influenced due to various stalk positions.

The author did not show up and the report was not given.

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The correlation coefficient on the total alkaloids curve was 0.9908 and the standard error of calibration was +/- 0.1681. The correlation coefficient for total nitrogen was 0.995 and the standard error of calibration was +/- 0.02.
A high degree of correlation was also achieved when the equations which were found were applied to the samples of the next set. The results are represented graphically in Figures 4 and 5.

FIGURE 4
RESULTS FROM TEST SET OF SAMPLES- TOTAL ALKALOIDS

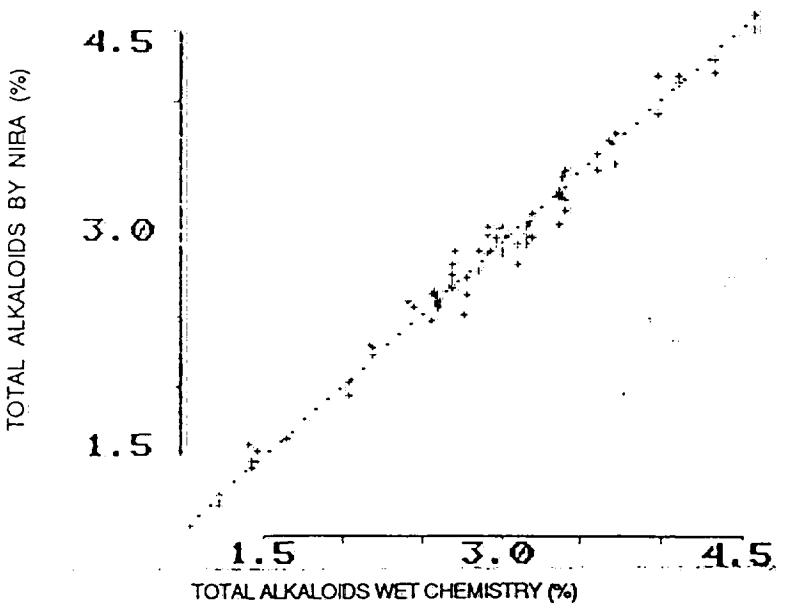
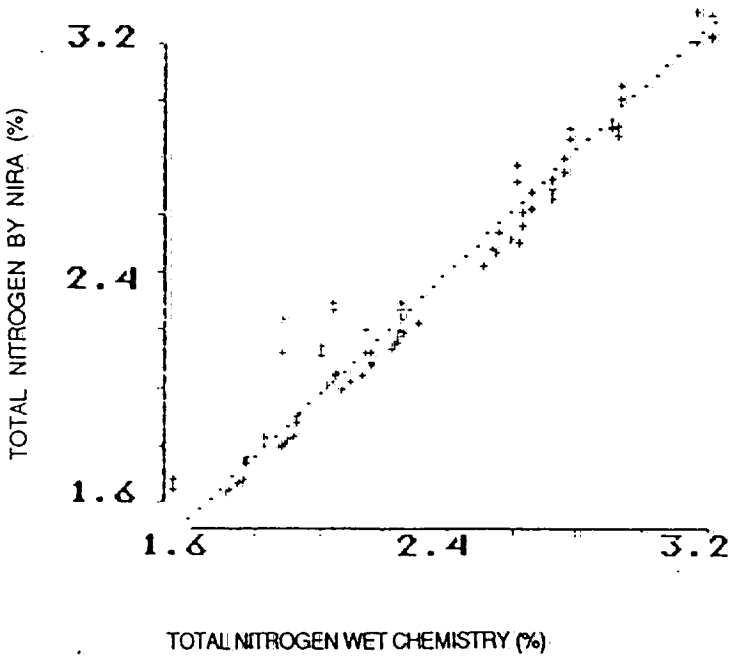


FIGURE 5
RESULTS FROM TEST SET OF SAMPLES-TOTAL NITROGEN



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variability in all three crops; grade A6 seems more similar to grade C than to grades A7 and A8. The mean vector of the chemical variables for each grade can be observed in Figure 5.

A generalized Hotelling test was conducted on the Mahalanobis distances among the 21 grades (Table 6), using the information from the first three PC to determine chemical equivalence between grades. Table 7 shows the results for some grades. The grade pairs D6-D8, C6-C7 and C6-A7 were equivalent among them.

The mean vectors of the three PC of each grade were analyzed with a hierarchical cluster method (Nearest Neighbor using Euclidian Distance) and the results obtained are shown on Figure 6. The groups formed by D, E, F, G confirm the consistency of these grades along the three crops. Groups A8, A6-C8-A7-C6-C7-B6, and B7-B8 show a deviation from the expected classification. A rigorous examination of these grades' samples which show inconsistency could lead to a re-classification or to a simplification or change in the grading criteria.

TABLE 6. MAHALANOBIS DISTANCE

	C8	F6	E8	D6	C8	D8	A8	C7	F7	E7	B7	C7	B7	A7	C6	F6	E6	D6	C6	B6	A6
A6	43.0	32.4	13.2	17.4	3.9	8.5	3.2	39.7	35.5	14.3	26.6	4.9	8.9	6.5	33.0	30.7	16.5	20.9	3.0	7.6	0.0
B6	42.7	13.5	14.3	3.4	5.9	1.7	13.8	38.9	14.8	12.7	6.5	1.7	2.0	3.3	32.9	12.7	21.0	4.5	2.1	0.0	
C6	31.3	15.7	7.1	6.0	1.1	2.0	5.3	28.3	17.8	6.8	12.2	0.2	3.2	0.3	23.0	14.7	11.5	8.3	0.0		
D6	34.9	3.2	16.6	0.2	11.4	3.7	24.1	31.0	2.8	11.8	0.5	5.9	5.1	11.6	26.5	2.8	22.3	0.0			
E6	7.8	19.3	0.9	16.6	5.7	15.8	7.2	5.6	24.7	1.7	28.3	11.0	20.9	11.8	4.8	19.4	0.0				
F6	22.8	0.5	16.2	3.1	11.2	3.3	20.6	20.5	0.6	9.9	3.5	11.3	11.1	10.9	17.3	0.0					
C6	1.5	18.4	8.2	23.6	15.3	22.6	18.6	1.2	23.0	5.5	32.4	21.1	28.2	24.8	0.0						
A7	33.1	29.0	7.5	8.9	1.2	3.5	3.8	30.6	22.5	8.1	16.1	1.0	4.6	0.0							
B7	39.2	13.7	16.0	4.0	6.3	0.5	12.7	36.2	13.7	12.3	8.8	2.8	0.0								
C7	29.1	13.1	6.6	4.0	1.4	1.4	6.6	26.0	14.0	5.7	9.4	0.0									
D7	40.3	3.5	21.7	1.3	16.3	6.8	31.2	36.6	2.6	16.3	0.0										
E7	9.7	16.1	1.0	9.2	3.3	8.2	7.9	7.4	13.6	0.0											
F7	28.6	0.4	20.4	3.7	19.4	10.9	34.9	25.6	0.0												
C7	0.7	20.2	9.2	28.0	19.7	29.2	24.6	0.0													
A8	25.6	36.5	6.2	19.9	2.5	10.8	0.0														
B8	32.2	16.3	11.4	2.5	4.1	0.0															
C8	22.2	16.2	3.1	8.6	0.0																
D8	31.7	3.5	13.6	0.0																	
E8	11.9	15.7	0.0																		
F8	23.3	0.0																			
C8	0.0																				

Tabla 7. Hotelling T^2 Generalyzed Multivariate Analysis of Variance

Pairs	D^2	F. Calculated
D6-D8	0.18	1.91
C6-C7	0.19	2.42
C6-A7	0.23	2.89
D6-D7	0.44	4.69
F7-F8	0.36	4.77
B7-B8	0.42	5.02
F6-F8	0.45	5.19
F6-F7	0.51	5.89
E6-E8	0.73	7.73

F (3,143) = 3.92

c. Classification According to Chemical Quality Parameters

A data file (Table 2) that contained the chemical analysis of 49 non-classified samples of Flue-cured, Burley, Black air-cured, and Extra air-cured tobaccos, was analyzed by a non-hierarchical cluster method, in order to evaluate the ability of this technique to group samples of similar chemical characteristics, using the first four PC containing 97.8% of the total population variance (Figure 7). Five of the six formed groups correspond clearly with the five types of tobacco, and only one sample was classified as a different group. This technique has a great potential to classify tobaccos of unknown nature, according to their chemical quality parameters.

CONCLUSION

Multivariate techniques represent a more powerful tool than the ones that have been used (univariate statistics) for the evaluation of tobacco grading systems, crops comparison and determination of equivalences among tobaccos. Although

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The BaP levels in the MS of the high-yield nonfilter cigarette are not positively correlated with the tar values, which is in agreement with previous findings (10). While BaP delivery in the MS of the full-flavored nonfilter cigarette reached a minimum at the 35-mL puff volume, BaP levels in the MS of an ultra low-yield cigarette (E) rose linearly with an increase in puff volume.

By comparison to data obtained without restricting the air vents of the perforated filter tip of cigarette B (6.1 % ventilation), blocking of the vents caused MS deliveries to increase by 1.3 - 13.1 % for tar, by 1.9 - 13.6 % for nicotine, by 14.3 - 30.2 % for NNN, by 23.5 - 33.3 % for NNK, and by 15.5 - 28.6 % for total TSNA. When the air vents of ultra-low yield cigarette F (76.8% ventilation) were blocked, the increased delivery of toxic and biologically active compounds in the MS of these cigarettes was even more significant (3.2- to 5.8-fold for tar, 2.4- to 4.1-fold for nicotine and 4- to 11-fold for individual and total TSNA), clearly showing different dynamics for different smoke constituents. By blocking air vents of the filter tips during smoking, a cigarette designed to deliver 1 mg tar will in effect yield 8 mg tar per cigarette.

We are currently studying the effects of various other smoking parameters on the smoke yields of tar, nicotine, and individual TSNA.

ACKNOWLEDGEMENT

The investigators appreciate the assistance of Ms. Lisa Biear, Ms. Yin Liu and Mr. Mark Kagan in performing the smoke analyses and thank Drs. L.P. Bush and H.R. Burton from the University of Kentucky, Agronomy Department, Lexington, KY 40546 for nitrate and nitrite analysis. This study is No. XCIII of the series "Chemical Studies on Tobacco Smoke". The research was supported by Grant CA-29580 from the U.S. National Cancer Institute.

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excellent for filtration selectivity of the acids. Thus cellulose acetate was far superior to the other materials, and polypropylene was judged to be the least effective.

Table II Dependence on Filter Material of Acid Delivery, Filtration Efficiency, and Selective Filtration Coefficient

Filter Material	Non	Cellulose (Neo-filter®)	Cellulose Acetate (f/d:3Y)	Polypropylene (f/d:7Y)
Pressure Drop (mmWG)		48	48	49
Delivery (μg/cig.)				
Formic acid	415	155	137	213
Acetic acid	946	380	366	482
Filtration Efficiency (%)				
Formic acid	–	63	67	49
Acetic acid	–	60	61	49
Dry TPM	–	42	39	36
Selective Filtration Coefficient				
Formic acid	–	1.57	1.85	1.25
Acetic acid	–	1.45	1.56	1.25

Tobacco Column : "Cherry", a commercial product of Japan Tobacco Inc.
Filter : Length 17mm, circumference 24.7mm
Neo-filter ®: Filter made from wood pulp non-woven sheet

Judging from the molecular structure of cellulose acetate it is reasonable to think that cellulose acetate is high in affinity to formic and acetic acid. So, in the case of cellulose acetate filters, the affinity between the cellulose acetate and the acids contributes in large part to the filtration selectivity. In cellulose filters, the high filtration selectivity is considered to be caused by the affinity between the moisture and the acids : cellulose is the highest of the three materials in moisture content.

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REFERENCES

1) Stedman, R. L. : Tobacco Sci. 8, 79 (1964)
2) Stedman, R. L., D. Burdick, I. Schmeltz : Tobacco Sci. 7, 166 (1963)

Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

warm years the Geudertheimer cultivars produce rather high nicotine contents.

The carbon monoxide contents from 8 to 10 ml per cigarette in the Geudertheimer cultivars are very low. They are comparable with the contents of the commercial low carbon monoxide brands.

The Geudertheimer cultivars have surprisingly low nitric oxide contents: they are in the region from 67 to 88 ug (micrograms) per cigarette.

BURLEY - CULTIVARS

Condensate, nicotine, carbon monoxide and nitric oxide. In the year 1987 the cultivars Badischer Burley E, Bursanica 217, Pereko, B 535, Burley 21, G 37 and Burley CA were planted. The Maryland cultivar MD 609 was planted for comparison purposes.

All Burley cultivars have in the stalk "leaf" condensate values between nineteen and twenty milligrams per cigarette. They are clearly outside the EEC-limitation. Therefore the Burley cultivars have no chance of getting any promotion by the EEC-authorities, too.

The Burley cultivars show very low nicotine contents similar to the Geudertheimer cultivars. Bursanica 217, Pereco and B 535 have a nicotine content of 0.25 mg per cigarette, the cultivar Badischer Burley E of 0.93 mg per cigarette, the cultivar Burley CA of 0.99 mg per cigarette and the cultivar Burley 21 of 1.33 mg per cigarette.

The Burley cultivars show very low carbon monoxide contents. The amounts between 8.6 and 9.8 ml per cigarette are somewhat lower than the amounts of the Geudertheimer cultivars. The nitric oxide conent in the smoke of Burley cultivars is low. It amounts from 84.8 ug to 211 ug per cigarette and is higher than those contents of nitric oxide ug found in Geudertheimer cultivars. The high content of 211 ug per cigarette is equal to the cultivars Badischer

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Burley E and only somewhat lower than that of the cultivar Maryland MD 609. This content equals to commercial brands with very high content of nitric oxide.

THE EFFECTS OF NITROGEN-FERTILIZER

For the Geudertheimer- and Burley-cultivars a N-fertilization of 180 kg. per hectare is recommended. The N-fertilization of more than of 180 kg. per hectare is a special experiment to show the effect of high N-fertilization in the smoke contents. In the case of zero fertilization the tobacco plant can only use the N-amount which is created by the mineralisation in the soil during the year. The harvesting grades of "leaf" and "tips" have been investigated in the tobacco leaf and smoke.

CONDENSATE

The condensate amounts of the Burley-tobacco with 250 kg N-fertilization per hectare is corresponding to those with 180 kg N per hectare. It has been found, that without N-fertilization the Burley-tobacco with 15.8 mg condensate per cigarette has already too much condensate according to the EEC demand. The Bad. Geudertheimer renders less condensate with 250 kg N per hectare (only 15.93 mg per cigarette). This amount seems to be false because the 180 kg N-fertilization creates already an amount of 19.31 mg per cigarette. In the Bad. Burley E ("tips") 20.6 mg condensate per cigarette are found with a fertilization of 250 kg N per hectare. In comparison to a zero fertilization the 250 kg N-fertilization makes the condensate content high, while in comparison with a 180 kg N-fertilization the condensate content is not so high. The cultivar Burlina 183, "tips", and the cultivar Burley NA, "leaf", - having 250 kg N-fertilization per hectare - are showing the same condensate amount of 20 mg per cigarette. The same has been observed in the cultivar Burling T89, "leaf", with a condensate content of 18.93 mg per cigarette and in the cultivar Burlina 183, "tips", with a condensate content of 20.23 mg per cigarette. Comparing the Burley-cultivars no differences are found with equal N-fertilization and within the same harvesting grade.

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FIGURE 1

PRINCIPAL COMPONENT ANALYSIS

DISPERSION ANALYSIS
FLUE-CURED TOBACCO GRADES - 1988 CROP

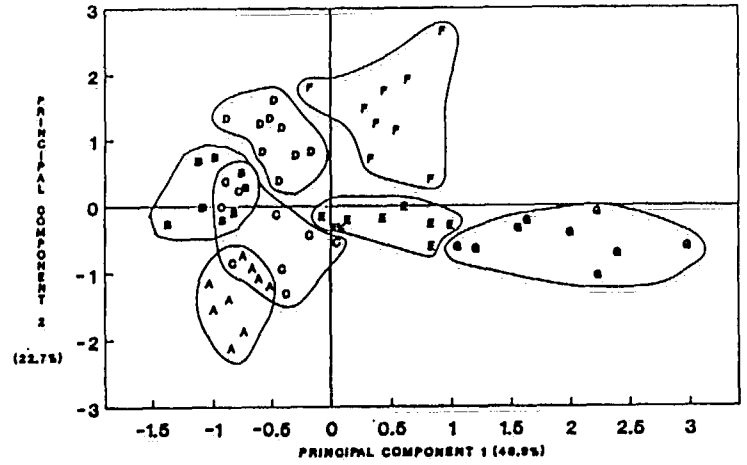


FIGURE 2. CHEMICAL VARIABLES REPRESENTED BY RICOUTL & FLURT'S STACIRIC FACES

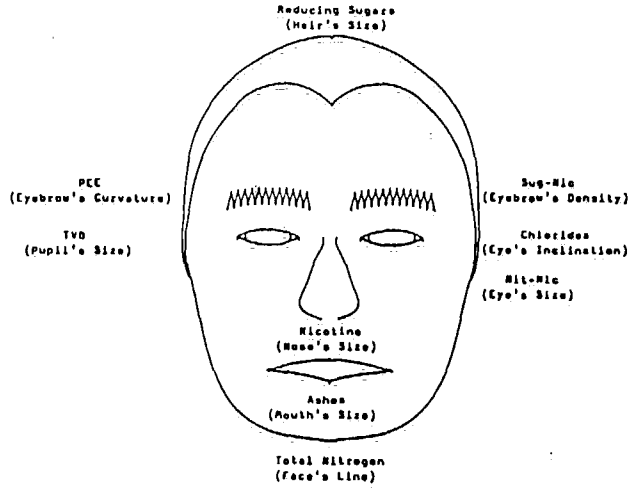


FIGURE 3

PRINCIPAL COMPONENT ANALYSIS

MEAN VECTORS
FLUE-CURED TOBACCO GRADES - 1988 CROP

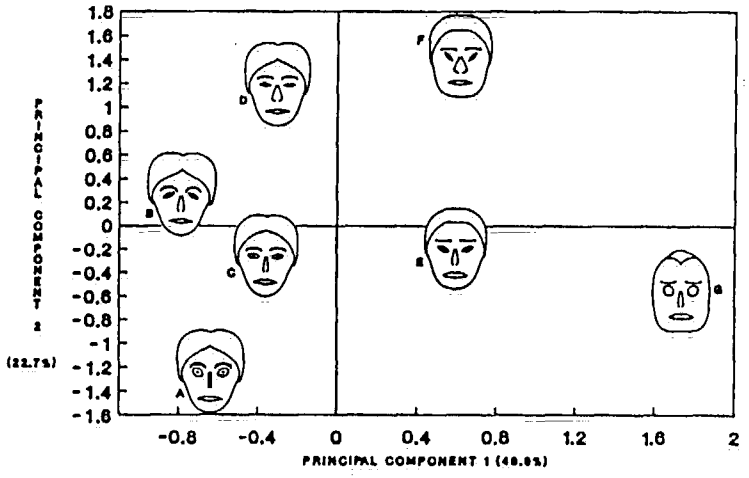
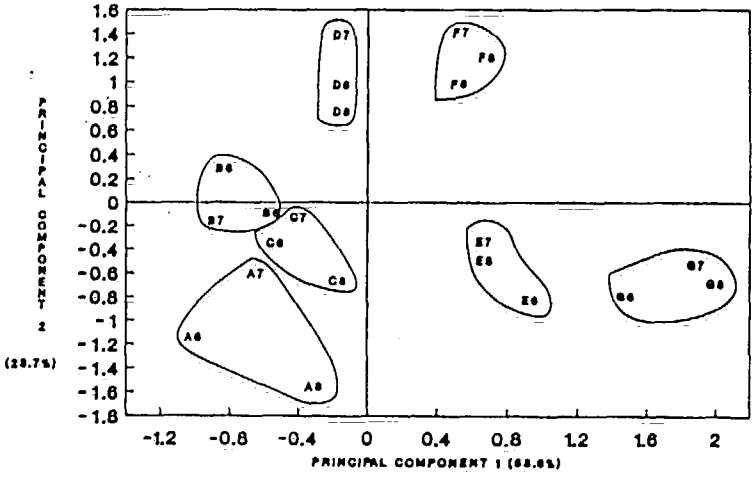


FIGURE 4

PRINCIPAL COMPONENT ANALYSIS OF FLUE-CURED TOBACCO

COMPARISON OF THE SAME GRADES BETWEEN 1986, 1987 AND 1988 CROPS



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DETERMINATION OF ORGANIC ACIDS IN TOBACCO SMOKE BY ION CHROMATOGRAPHY

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SUMMARY

An ion chromatographic procedure was applied to the determination of organic acids in tobacco smoke. Seventeen carboxylic acids were identified positively or tentatively in this study. Formic and acetic acid were the predominant organic acids in the smoke. Examined were the filtration efficiency and the filtration selectivity of the filters of cellulose, cellulose acetate and polypropylene for formic and acetic acid. Cellulose acetate was the highest and polypropylene was the lowest in both filtration efficiency and filtration selectivity for each acid.

INTRODUCTION

The aroma and taste of tobacco are greatly affected by the organic acids in tobacco smoke (1). The composition of the acidic fraction of the smoke has been determined in both quality and quantity by gas chromatography (2-7). The gas chromatographic procedure involved complicated pretreatments such as a simultaneous extraction and methylation or trimethylsilylation. A more convenient and rapid analytical procedure has been desired.

Recently, it was reported that ion chromatography can be used to analyze a wide range of organic acids (8). Baker P.G. and co-wokers have reported using ion chromatography to measure malic, oxalic, and citric acids in tobacco (9).

The research reported here is first a study on the application of ion chromatography to organic acid determination in tobacco smoke, and second a study on filtration of acidic components in the smoke for various filter materials using the ion chromatographic analytical procedure.

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opening of the Japanese market to foreign imports, especially from the U.S.A., has led to major increases in the production of carbon-containing filters. In parallel with the necessary improvements in production techniques to meet this demand, Filtrona have also been developing new types of adsorbent filter.

Testing methods for Vapour Phase active filters include specific compound tests e.g. for formaldehyde and HCN, carried out on whole smoke because they do not conform to the phase partitioning obtained with Cambridge filters. However, for general tests of activity, gas chromatographic separation of organic vapour phase compounds has usually been used. In common with many other laboratories, we used packed column methods for many years, and reasonable resolution could be obtained with carefully selected stationary phases, used at high loadings on columns up to 4 metres long. These methods had the disadvantages of fairly short column life, the necessity of matched column pairs because of high bleed rates, and long analysis times. In recent years, the development of bonded phases on fused silica capillary columns has provided better separating power combined with much greater column stability and lower analysis times.

METHOD

Cigarettes were smoked to tip + 8mm butt through a Cambridge filter holder on a Filtrona SM 302 smoking machine. Eight cigarettes were smoked per analysis the combined vapour phase being collected in a single bag made from biaxially orientated polypropylene/polyester laminate. Samples were analysed on a temperature programmed Carlo Erba Vega GC equipped with a Shimadzu MGS4 gas sampling valve with a 0.5cm^3 sample loop, a flame ionisation detector and a 20m x 0.32mm Poraplot Q fused silica capillary column, with a film thickness of 10µm.

The temperature programme was as follows: (i) 40°C (hold min) to 90°C at a rate of 45°/min; (ii) 90°C to 205°C (hold 1 min) at a rate of 5°/min; (iii) 205°C to 225°C (hold 5 min) at a rate of 45°/min. The detector temperature was 240°C.

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NICOTINE

The cultivar Bad. Burley E, "leaf", having a N-fertilization of 250 kg per hectare, is creating a high nicotine amount of 4.8 mg nicotine per cigarette. Without N-fertilization a low content of 0.62 mg nicotine per cigarette has been found. In the cultivar Bad. Burley E, "tips", the content of 2.72 mg nicotine per cigarette has been found without N-fertilization and in the "leaf", with a N-fertilization of 250 kg. per hectare the same amount of nicotine as in the "tips" without N-fertilization. In this experiment it is documented that without N-fertilization low nicotine contents are found. The Burlina-cultivars with the special cultivar T89 have been found with high nicotine contents, the other special cultivar NA shows low to middle nicotine content with a N-fertilization of 250 kg per hectare. That is the reason why Burlina T89 is a high-level nicotine cultivar and the Burlina NA is a low-level cultivar. In the Burlina 183 cultivar a low to middle amount has been found. All Burlina-cultivars can be clearly differenciated according to their nicotine content.

CARBON MONOXIDE

Different N-fertilization is influencing the carbon monoxide content only slightly. A comparison between the N-fertilization of 250 kg N per hectare and no fertilization at all renders the same carbon monoxide content of 10.6 ml per cigarette. This content equals to the content of the cultivar Burlina 183 with a N-fertilization of 250 kg per hectare.

NITRIC OXIDE

The nitric oxide amounts are directly correlated to the N-fertilization. The variation without N-fertilization has been found in the cultivar Bad. Burley E, "leaf", with the lowest amount of 61.9 mg nitric oxide per cigarette, the variation with 250 kg N per hectare rendered 231 ug nitric oxide per cigarette. The sample with 180 kg N per hectare has been found with 211 ug per cigarette. The cultivar Burlina T89, "leaf", shows a very high content of 206 ug nitric oxide per cigarette with a N-fertilization of 250 per hectare. 180 kg N per hectare create a nitric oxide content of 94

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

RESULTS AND DISCUSSION

Identification of Acids : Chromatograms of a typical cigarette smoke sample eluted with the 2.0 mM phosphoric acid are shown in Figure 1, and the substances identified are listed in Table I. About forty substances in the smoke were detected together through conductivity and UV detection, and seventeen carboxylic acids were identified positively or tentatively in this study. Among these substances in the table, ß, ß'-thiodipropionic acid has not been found in preceding articles, so it is necessary to study further using other identification methods in addition to retention time.

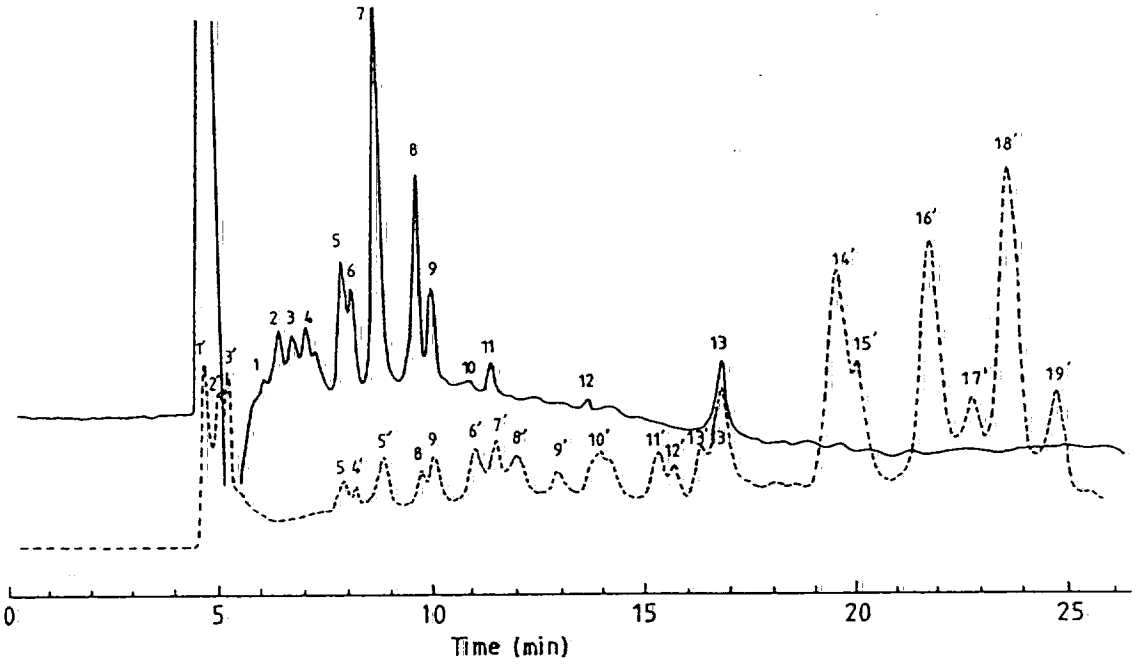

Fig. 1. Ion Chromatogram of Organic Acids in Cigarette Smoke
Detector : Conductivity ———, UV --------

In the longer retention time region, several strong peaks were found using UV detection, though the corresponding ones were scarcely found in conductivity detection. It is considered that the peaks are those of substances in whose molecules the weight ratio of the acid group is low and such structures as unsaturated bonds and /or aromatic rings sensitive to UV are contained. Further investigation is in progress on three peaks 14', 16', and 18' by MS analysis for the fraction collected.

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Figure 1

TIP MENTHOL

UNSMOKED CIGARETTE

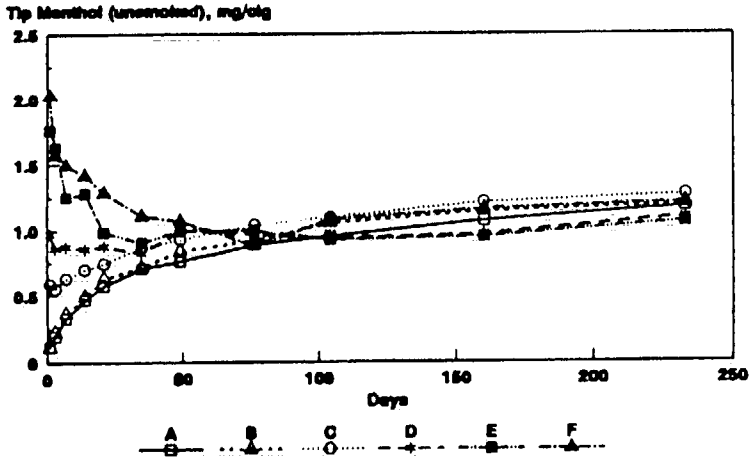

Figure 2

COLUMN MENTHOL

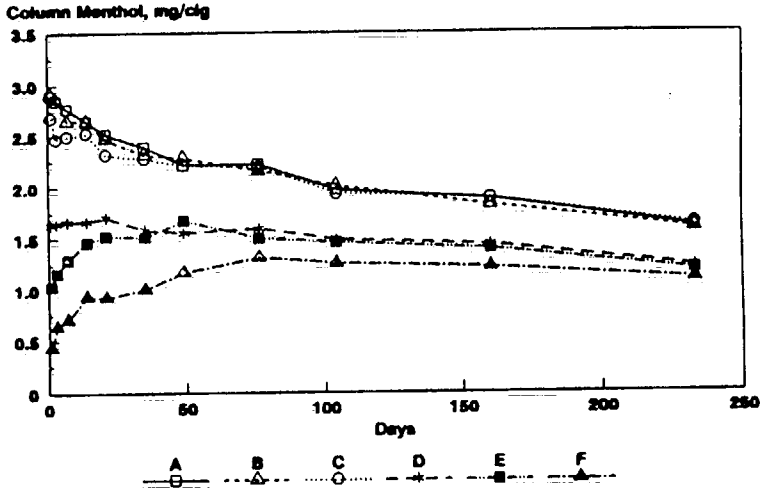

Figure 3

MENTHOL DELIVERY, CORRECTED

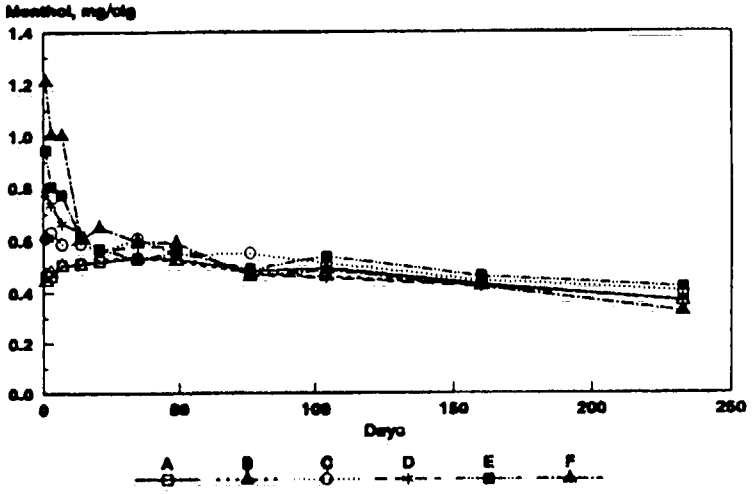

Figure 4

FILTER NET MENTHOL GAIN OR LOSS:

PRIMARY CIGARETTES

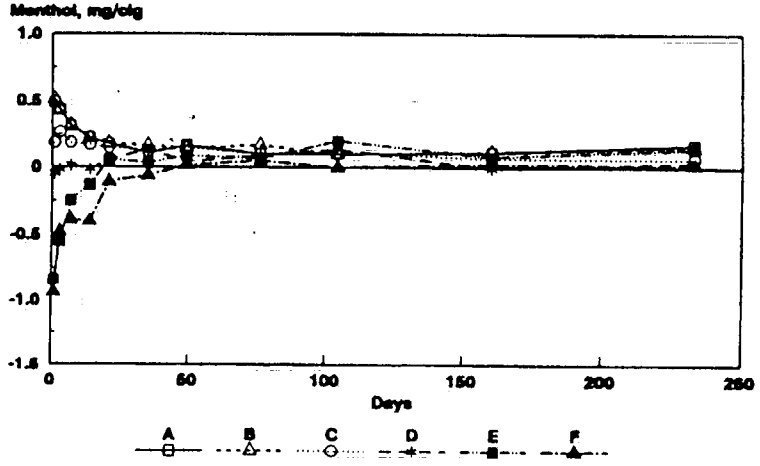

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Table 4: Selenium content in main stream smoke of cigarettes
(Burley and standard mixture)

Cigarette B_0, R_{20}	Tobacco (µg/cig)	Crude condensate (µg/g)	Transfer %
$B_0F_{32}P_{25}$	0.079	0.0087	11.0
$R_{20}F_{24}P_{10}$	0.068	0.011	16.2
$R_{20}F_{32}P_{25}$	0.072	0.008	11.1
$R_{20}F_{44}P_{42}$	0.073	0.006	8.2
$R_{20}F_{44}P_{70}$	0.070	0.006	8.6
$R_{20}F_{44}P_{150}$	0.069	0.004	5.8
$R_{20}F_{44}P_{100}$ + 7 ug Se/cig	7.4	0.267	3.6

B_0 = Burley
R_{20} = Standard mixture
F = filtration (%)
P = porosity CU

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

Furthermore, the cultivation of tobacco in the EEC is restricted to regions with well defined cultivars and certain yields. The cultivars Virgin, Geudertheimer and Burley are only of interest for the German plantation. Seventeen German cultivars have been analyzed in leaf and smoke for: nitrate, alkaloides, condensate, nicotine, carbon monoxide and nitric oxide. In previous investigations the cultivar Virgin D showed a low rate of nitric oxide. Therefore no German Virgin cultivar has been analyzed. Six Geudertheimer cultivars, - lugs and leaf, N-fertilizer 180 kg/ha -, eleven Burley cultivars, - leaf and tips, N-fertilizer 180 kg/ha and the cultivar Badischer Burley E, - N-fertilizer variation 0 kg and 250 kg/ha have been investigated. All tobacco samples were unfermented. One thousand six hundred and twenty cigarettes, well defined in paper, filling power, and hardness were made by hand, under standardized conditions: twenty-seven samples, sixty cigarettes per sample. Nitric oxide has been determined separately in a second smoking procedure.

GEUDERTHEIMER CULTIVARS

Condensate, nicotine, carbon monoxide and nitric oxide. The Geudertheimer cultivars Geudertheimer III, Badischer Geudertheimer W, Badischer Geudertheimer K and Perega 234 were planted in 1987 in Forchheim. The stalk positions "lugs" and "leaf" were only air dried.

The EEC limitation to 15 mg condensate per cigarette is fulfilled for the cultivars Geudertheimer III and Badischer Geudertheimer W in the stalk position "lugs". In the stalk position "leaf" no Geudertheimer cultivar is within this limitation: all cultivars have values of 19 mg per cigarette and have therefore clearly 4 mg condensate more than 15 mg.

The nicotine level in the stalk position "lugs" of the Geudertheimer cultivars is very low. The stalk position "leaf" has with 0.19 mg nicotine per cigarette the lowest nicotine content. The tobacco year 1987 showed low temperatures combined with wet and rainy weather. Therefore the low nicotine content reflects more the weather conditions than the Geudertheimer properties: in dry and

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TOBACCO-SPECIFIC NITROSAMINE DELIVERY IN THE MAINSTREAM SMOKE OF HIGH- AND LOW-YIELD CIGARETTES SMOKED WITH VARYING PUFF VOLUMES

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Naylor Dana Institute for Disease Prevention
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SUMMARY

In view of changes in human smoking patterns with the introduction of low-tar cigarettes it was of interest to determine how the puff volume affects the mainstream (MS) yields of tobacco-specific nitrosamines (TSNA). Six U.S. blended cigarettes with a wide range of FTC tar and nicotine yields were machine-smoked with puff volumes of 25, 30, 35, 40, and 45 mL, respectively. Collection of MS and determinations of total particulate matter (TPM), water, nicotine, benzo(a)pyrene, as well as of TSNA were performed according to published methods. While tar, nicotine, TSNA, and BaP content of MS of low- and ultra low-yield cigarettes were found to rise with increasing puff volume, TSNA levels in MS of full-flavor, high-yield cigarettes reached a peak when cigarettes were smoked with a 35-mL puff. Blocking the air vents during smoking of cigarettes with perforated filters doubles the increases of TSNA yields in MS compared to increases in the yields of tar and nicotine. Our findings underscore that the yields of TSNA in MS are greatly affected by the smoking intensity.

INTRODUCTION

Smoking low-yield cigarettes compels the smoker to change smoking behavior. Smokers who switch brands, often draw larger

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EXPERIMENTAL METHOD

Six blends were created, including one which contained bright tobacco and five others having a 1:1 proportion of the same bright and reconstituted tobaccos. The first of the reconstituted blends, RP, was made using a paperlike process, while the other two, R1 and R2, were made using slurry type processes.

The RPc and R2c blends were made using the same bright tobacco, while a 20%(w:w) of a sauce was added at room temperature to the reconstituted tobacco used in the RP and R2 blends before blending. The sauce was a solution of Zn (NO3)2 (3:7 w:w) in a mixture of Propylglycol, Benzylalcohol and Ethanol (3:3:1 w:w). The cased reconstituted tobacco was then left overnight.

The six blends were processed in the same conditions and were cut to a width of 0.8 mm and then used to produce cigarettes with a LabMax. The tobacco of these cigarettes was sieved (4) and 7 fractions were collected. Several anions were determinated by HPLC and Propylglycol, Glycerine on Benzylalcohol were analized by GC. Experimental details can be found elsewhere (5, 6, 7, 8).

RESULTS

Some of the results for complete blends obtained are found in Table 1.

Nitrates experienced an increase in every case compared with the Control. An increase was also detected in RPc and R2c for nitrate ion, previously added for use as a tracer in the experimental sauce. The concentration of phosphate in the R1 blend increased as much as 5 times the average value of the others. The high concentration of phosphate ion suggests that it can be used as a good tracer for the presence of this type of reconstituted tobacco in a blend.

Table 1. - Chemistry of the reconstituted blends.

	Cl	NO3	PO4	SO4	Pg	Bz	Gl
Control	1.07	0.00	0.64	2.52	0.00	0.00	0.00
R1	1.37	1.06	2.44	2.52	0.54	0.00	0.66
RP	1.03	0.41	0.49	2.12	0.00	0.00	0.00
R2	1.43	0.97	0.54	1.81	1.39	0.00	1.58
RPc	0.93	1.37	0.36	1.94	1.77	0.95	0.00
R2c	1.61	2.50	0.55	1.85	4.20	2.20	1.19

If we consider the RPc and R2c blends, that were made with sauces for this study, it can be seen that the concentration of propylglycol has increased in both blends.

Now let us consider the distributions of compounds in the different fractions.

In figure 1 we see the normalized distributions of the shred size for the different blends.

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Formic and acetic acid were the predominant organic acids in the cigarette smoke studied in this paper as noted in the preceding article (7).

Table I Acidic Compounds in Cigarette Smoke (refer to Fig. 1)

Conductivity Detection			UV Detection		
Peak No.	Compounds	Rt. Time (min.)	Peak No.	Compounds	Rt. Time (min.)
1	Succinic acid	6.2	1'	Oxalic acid	4.7
2	Malic acid	6.4	2'	Malonic acid	5.0
3,4	Unknown		3'	Oxalacetic acid	5.2
5	Glycollic acid	7.8	5	Glycollic acid	7.8
6	Itaconic acid	8.1	4',5'	Unknown	
7	Formic Acid	8.6	8'	Acetic acid	9.6
8	Acetic acid	9.6	9	ß,ß'-Dithiopropionic	10.0
9	ß,ß'-Dithiopropionic	10.0		acid	
	acid		6'	Unknown	
10	Unknown		7'	Acrylic acid	11.6
11	Propionic acid	11.4	8'	Phthalic acid	12.0
12	n-Butyric acid	13.6	9',10'	Unknown	
13	Pyromucic acid	16.9	11'	Methacrylic acid	15.2
			12',13'	Unknown	
			13	Pyromucic acid	16.9
			14'~19'	Unknown	

Filtration Efficiency and Selectivity : The filtration efficiency of tobacco filter materials for formic and acetic acid was examined for cellulose, cellulose acetate, and polypropylene.

Table II shows the quantitative data of formic and acetic acid delivery for cigarettes with and without filters, as well as the filtration efficiency of each filter for the two kinds of acid and for the dry TPM (total particulate matter). The selective filtration coefficient for the acid was also calculated.

For the filtration efficiency, cellulose acetate was a little bit higher than cellulose, and polypropylene was the lowest. However, all of the fibrous materials examined were

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Table I

Comparison of New Method Versus Current Method

Sample	CO mg/cig	NO µg/cig	CH_3CHO µg/cig	HCN µg/cig	Puff Count
2R1F					
New	20.3	295	1192	184	10.5
Current	20.1	282	1051	214	10.0
% Difference	+1	+5	+13	-14	
1R4F					
New	10.5	279	670	72	8.9
Current	10.7	285	646	102	9.1
% Difference	-2	-2	+4	-29	
2R1					
New	20.9	297	1235	232	12.4
Current	21.0	300	1147	251	12.3
% Difference	-1	-1	+8	-8	

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ACKNOWLEDGEMENTS

The authors deeply appreciate the contributions from Woody Early, Bob Fenner, Horace Hartley, Charles Harward, John Lephardt, Jim Lyons-Hart, Jeff Sampson, Ken Shafer, Gunars Vilcins, Jim Washington, and Ed Wickham.

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DETERMINATION OF TOTAL ALKALOIDS AND TOTAL NITROGEN BY NEAR INFRARED REFLECTANCE SPECTROSCOPY

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SUMMARY

Near infrared reflectance spectroscopy (NIR) can be used to increase the rapidity with which the level of chemical constituents in tobacco can be determined.

One hundred and twenty samples of Virginia tobaccos were scanned with computerized NIR spectrophotometer (TECHNICON 450 R +) to study the relationship of intensity of reflectance spectra to the total alkaloids and total nitrogen content of the samples.
A multiple linear regression model was used to select the most appropriate wavelengths for the measurements.

The equations for

TOTAL ALKALOIDS (%) = 1.862 + 1.77 (log 1/R)546 - 44.93 (log 1/R)2310 + 220.7 (log 1/R)2270 -222.0 (log 1/R)2230 + 691.6 (log 1/R)1818 - 512.2 (log 1/R)1759 + 8.614 (log 1/R)1940 - 609.2 (log 1/R)1734 - 34.2 (log 1/R)1722 + 807.8 (log 1/R)1680

and for

TOTAL NITROGEN (%) = 4.941 + 1.677 (log 1/R)546 - 40.64 (log 1/R)2310 - 61.03 (log 1/R)2208 + 118.15 (log 1/R)2180 + 317.96 (log 1/R)1982 - 346.95 (log 1/R)1818 +805.3 (log 1/R)1778 - 92.66 (log 1/R)1759 + 13.8 (log 1/R)1940 + 560.32 (log 1/R)1734 - 617.1 (log 1/R)1722 - 34.15 (log 1/R)1445

give results in good agreement with standard chemical methods.The coefficient of correlation for total alkaloids (R) was 0.9908 and the standard error of calibration was +/- 0.1681. For total nitrogen coefficient of correlation R was 0.995 and the standard error was +/- 0.022.

Using these equations the total alkaloids and the total nitrogen in an independent set of samples could be determined with relative error, against wet chemistry, of +/- 6.2 % for total alkaloids and +/- 5.5 % for total nitrogen.

INTRODUCTION

Requirements concerning a knowledge of the chemical and physical characteristics of raw materials and/or final products are very important in any industry, and thus also in the tobacco processing industry. There are numerous laboratory techniques which, by their range of application, their accuracy and their speed, meet the requirements of the industry.
Methods and/or techniques such as Liquid Chromatography, Gas Chromatography, AAS or emission methods such as ICP as well as automatized chemical methods are accurate, relatively fast and have a wide range of application. The step which slows down analyses carried out by the above mentioned techniques is the preparation of samples. During sample preparation, the sample has to be destroyed, dissolved and/or extracted, so this step of the analysis is a factor limiting the speed with which the analysis is performed.

An analysis technique which has been attracting attention since the early sixties is the analysis of the chemical composition of a sample based on absorption changes of reflected near infrared radiation from the sample. The advantages of this technique are the shorter time needed to prepare the samples, the speed of the analysis itself, its accuracy and reproducibility, as well as its non-destructiveness.

Analysis of the total nitrogen, alkaloids, protein nitrogen, total reducing sugars, polyphenols and some inorganic components have already been made on tobacco (1 - 4).

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TABLE 2

NICOTINE, TSNA AND BaP IN MAINSTREAM SMOKE[a]

CIGARETTE	PUFF ml	TPM	TAR	NIC	NAT	NAB	NNN	NNK	Total TSNA	BaP
		mg/cig			ng/cig					
A:										
NF, SP, 85 mm	25	25.7	22.8	1.41	131	24	118	64	337	43.5
FTC TAR 24; NIC 1.5	30	28.3	23.7	1.36	134	16	131	74	356	44.4
VENTILATION: N/A	35	26.8	23.6	1.37	190	24	177	101	492	23.0
BUTT LENGTH: 23 mm	40	34.9	29.8	1.69	173	24	164	97	458	34.2
AVG. WT: 1.1136 g	45	39.7	33.9	1.74	129	18	124	79	349	41.0
B:										
F, SP, 85 mm	25	17.7	14.7	0.84	136	11	125	59	332	
FTC TAR 17; NIC 1.1	30	19.2	16.6	0.88	140	11	131	62	344	
VENTILATION: 6.1 %	35	23.9	19.0	0.95	167	12	162	75	417	
BUTT LENGTH: 28 mm	40	26.7	19.8	1.02	140	10	132	75	357	
AVG. WT: 0.9731 g	45	28.7	22.0	1.07	129	11	135	78	347	
C:						[b]				
F, SP, 85 mm	25	7.4	6.6	0.47	74	ND	72	37	183	
FTC TAR 8; NIC 0.6	30	8.5	7.5	0.44	77	ND	77	40	194	
VENTILATION: 35.3 %	35	9.9	8.6	0.52	91	10	81	48	230	
BUTT LENGTH: 35 mm	40	12.6	11.4	0.61	96	11	88	49	244	
AVG. WT: 0.9260 g	45	14.6	13.0	0.63	91	ND	89	49	229	
D:										
F, SP, 85 mm	25	7.7	7.1	0.04	37	6	24	25	93	
FTC TAR 7.6; NIC 0.03	30	9.2	8.6	0.04	46	8	31	31	116	
VENTILATION: 26.6 %	35	11.2	10.2	0.04	50	9	34	36	129	
BUTT LENGTH: 35 mm	40	12.0	10.6	0.05	55	9	36	39	138	
AVG. WT: 0.8855 g	45	13.2	11.6	0.05	58	9	40	42	149	
E:										
F, SP, 85 mm	25	0.9	0.8	0.06	12	2	10	5	28	2.6
FTC TAR 1; NIC 0.1	30	1.2	0.9	0.08	15	2	11	5	34	3.8
VENTILATION: 73.3 %	35	2.0	1.5	0.11	21	3	17	8	49	5.4
BUTT LENGTH: 33 mm	40	2.2	1.8	0.14	26	5	23	10	64	6.4
AVG. WT: 0.8045 g	45	2.4	2.1	0.16	30	4	26	12	72	9.0
F, SP, 85 mm	25	1.0	1.0	0.07	6	1	6	3	16	
FTC TAR 1; NIC 0.1	30	1.4	1.3	0.10	8	2	8	4	22	
VENTILATION: 76.8 %	35	1.7	1.3	0.14	14	2	14	6	37	
BUTT LENGTH: 34 mm	40	2.5	2.0	0.18	16	3	15	6	41	
AVG. WT: 0.7619 g	45	3.2	3.0	0.20	21	4	21	9	54	

a Filter cigarettes smoked with open air vents

b ND, not detected

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MENTHOL BEHAVIOR IN THE FILTER CIGARETTE: I. THE DEPENDENCE OF MENTHOL MIGRATION AND DELIVERY ON THE SITE OF APPLICATION. Lance J. Deutsch, Filter Products Division, Hoechst Celanese Corporation, P. O. Box 32414, Charlotte, North Carolina, 28232 USA.

SUMMARY

The behavior of menthol within a filtered cigarette was studied over time as a function of site of menthol application to the cigarette. Migration of menthol within the cigarette followed the expected pattern; menthol moved from areas of high concentration to low concentration. The plasticized filter continued to absorb menthol, which became largely unavailable to the smokestream, except for a small amount delivered via elution. Menthol deliveries were site-dependent intially but exhibited no significant differences after the menthol migration reached a steady state. Individual contributions of the filter and the tobacco column were determined and discovered to be independent of each other.

INTRODUCTION

Menthol is one of the most widely used flavorants in the tobacco industry. The volatility of menthol is a problem in terms of efficient application to the cigarette, retention during storage, and delivery upon smoking. Typical rates of utilization of delivered menthol relative to that applied to the cigarette range from 10 to 15%. Although these rates are low, the greater concern is variability over time, which can have a negative impact on smoker satisfaction.

This study was undertaken to determine both the diffusion of menthol within the cigarette and delivery of menthol in the mainstream smoke as a function of site of application to the cigarette and as a function of shelf life. This was accomplished by studying several sets of cigarettes prepared by shifting menthol application from tobacco columns to filter tip in 25% increments. The cigarettes were then allowed to age in sealed packs and sampled at intervals for smoking.

In a corollary to this study, mentholated filter tips were removed from their tobacco columns at controlled intervals, attached to non-mentholated tobacco columns, and smoked. Similarly, mentholated tobacco columns were detached from their filter tips and smoked on non-mentholated filter tips. In this way, the individual contributions to menthol delivery from the tobacco columns and the filter tips could be investigated.

EXPERIMENTAL

Six sets of cigarettes were manufactured to identical specifications (Table 1), with the exception of the percentage of menthol applied to the filter tips vs. the tobacco columns. Nominal menthol application was 3 mg per cigarette. A non-mentholated cigarette was also produced as a control and as a source of non-mentholated filter tips and tobacco columns. The cigarettes were non-ventilated. The filters were 21 mm in length and consisted of standard cellulose acetate tow bonded with 6% triacetin. The tobacco columns were 63 mm in length and contained a typical American tobacco blend.

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puffs of smoke from cigarettes that deliver lower nicotine yields than from their former brand (1). Changing the standardized parameters of machine smoking (35 mL puff volume; 2 seconds puff duration; 60 seconds puff frequency) to conditions more proximate to the behavior of low-yield cigarette smokers (47 mL puffs of 2.4 sec. duration taken every 44 seconds) has shown that tar and nicotine yields increase 15- to 39- fold and 8- to 19-fold respectively (2). Another study revealed that puff frequency had a greater effect on mainstream smoke (MS) delivery of alkaloids than variation of puff volume (3). An investigation of the MS yields of selected smoke constituents of six German cigarettes has shown that puff volume and frequency not only affect tar and nicotine delivery but also have a significant influence on the yields of tobacco-specific nitrosamines (TSNA; 4). In the range of 20-50 mL the relationship between puff volume and MS yields of individual TSNA was found to be linear (5).

Smokers of ultra low-yield cigarettes also have a tendency to block air vents in the filter tips with their lips and/or fingers. This increases smoke yields from 1 mg to 16 - 29 mg tar, thus counteracting the purpose of the ultra low-yield design of this cigarette (6).

The objectives of the current study were: (i) to determine the effect of smoking conditions (with puff volume and hole-blocking of filter vents as variables) on delivery of TSNA and benzo(a)-pyrene in the MS of six U.S. blended cigarettes with a wide range of FTC tar and nicotine deliveries; and (ii) to examine the relationship between TSNA in MS and their precursors in tobacco.

MATERIALS AND METHODS

One nonfilter and four filter-tipped brands of 85-mm U.S. blended cigarettes were purchased in 1990 from retailers in Westchester County, NY. Filter cigarette D (six samples) was

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ug per cigarette in the cultivar Bursanica, "leaf". This amount equals to the low content of 93 ug nitric-oxide per cigarette of the cultivar Burlina 183, "tips", with 250 kg N-fertilization per hectare. The cultivar Burlina NA has been found with a slightly increased nitric oxide content of 140.9 ug per cigarette with a N-fertilization of 250 kg per hectare. The cultivar Bad. Geudertheimer is producing an amount of 170.4 ug nitric oxide per cigarette, with a N-fertilization of 250 kg per hectare, 180 kg N are producing only 67.8 ug nitric oxide per cigarette. All amounts are related to the "leaf". An exaggerated N-fertilization has been found to create the double nitric oxide content in the cultivar Bad. Geudertheimer. Very high nitric oxide amounts hae been found in the cultivar Bad. Burley E, "tips", in the variation without N-fertilizer with 277.1 ug nitric oxide per cigarette and in the "leaf" with 250 kg N per hectare with 231 ug nitric oxide per cigarette.

NITRATE IN TOBACCO LEAF AND NITRIC OXIDE IN TOBACCO SMOKE

The components of the tobacco smoke are influenced by amount and composition of substances found in the tobacco leaf. In the cultivar Bad. Burley E with a N-fertilization of 250 kg. per hectare a nitrate amount of 1.2 % has been found, creating a nitric oxide amount of 231.6 ug per cigarette. Therefore it is now clearly seen, that the cultivar Bad. Geudertheimer creates a high nitric oxide content of 170.4 ug per cigarette with a N-fertilization of 250 kg per hectare and a nitrate content of 1.1 % in the leaf: the same nitrate content of 1.1 % nitrate is found in the leaf of the Bad. Burley E cultivar. This concentration is responsible for the nitric oxide content. The cultivars Burlina T89 and Burlina NA have been found to render a nitrate amount of 1.1 % or 0.9 % with a N-fertilization of 250 kg per hectare, which correlates to the high nitric oxide contents of 206.3 ug and 140.9 ug per cigarette.

NICOTINE AND NORNICOTINE IN THE TOBACCO LEAF

Independently of the cultivars low nicotine contents in the tobacco leaves have been found. Only the cultivar Burlina T89 has been found with a slightly higher content of 1.58 % nicotine compared to the cultivar Bad. Burley E with a content of 1.3 % nicotine and

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

RESULTS AND DISCUSSION

As shown in Table 1 there are no significant quantitative differences in individual or total alkaloids in the cigarette tobaccos of the studied brands, except for De-Nic brand (D) which had been de-nicotinized by supercritical fluid extraction (SCFE). This cigarette shows also significant differences in nitrate and nitrite nitrogen when compared to the other brands. In spite of low levels of nicotine, there were measurable amounts of individual and total TSNA in tobacco of cigarette D though they were somewhat lower than those in the tobacco of the other cigarette brands. This observation suggests that the SCFE does not remove all TSNA and their precursors while it removes nicotine to a significant extent.

The tar and nicotine yields in the MS of all six cigarette brands (Table 2) rise with increasing puff volumes. The MS of the de-nicotinized cigarette contained less nicotine than that of both ultra low-yield cigarettes. The levels of NNK, NNN, and total TSNA in MS of low- and ultra low-yield cigarettes, which were smoked without restriction of air vents in the filter tip, rise linearly with increasing puff volume, while the yields of these compounds in the MS of a full-flavor high-yield cigarette, both with and without filter tip, are the highest at 35-mL puff volume. Even though the nicotine content of cigarette D was very low (0.4 mg/g) there were measurable yields of TSNA in its MS. Nevertheless, these were only about half as much as those in the MS of cigarette C which yields about the same amount of tar. The occurrence of TSNA in MS of the De-NIC cigarette suggests that secondary amine alkaloids (nornicotine, anatabine, and anabasine) as well as the concentrations of preformed TSNA in toboccao play an important role in TSNA delivery during smoking. As expected, the levels of TSNA in MS decrease with an increase in the degree of ventilation in the cigarette filter tip.

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

EXPERIMENTAL

Ion Chromatography : The study was performed on a Model IC-500R (Yokokawa-Hokushin Electric Co.) ion chromatograph equipped with a conductivity and a UV detector. Samples were analyzed on a 4 mm ø x 250 mm SCS-5 anion separator column. A 2.0 mM aqueous phosphoric acid solution was used as an eluent at a flow rate of 1.0 ml/min. The column temperature was maintained at 45 °C.

Reagents : All solutions were prepared with deionized water (conductivity > 18 MΩ/cm). All chemicals used were of reagent grade.

Method of Collecting Smoke : Cigarettes available on the market were smoked under standard conditions (1 puff/min, 2 sec/puff, 30 mm in butt length) with a Filtrona constant flow type smoking machine. The smoke was collected in a cold trap cooled with dry ice-methanol.

Extraction of Acids : One hundred ml of deionized water was added into the trap containing the smoke condensate of 10 cigarettes, and the trap was shaken for 30 minutes on a shaker. The aqueous extract was passed through a 0.5 µm membrane filter after shaking.

Identification of Acids : Acids in the smoke were identified by comparing their ion chromatographic retention times with those of authentic compounds.

Calculation of Filtration Efficiency and Selective Filtration Coefficient for Acids :
The filtration efficiency of a filter made of various materials for formic and acetic acids was calculated by the following equation.

$$Ex(\%)=[Wu(x)-Wf(x)]x100/Wu(x)$$

where Ex is the indirect filtration efficiency for component x, Wu(x) is the weight of component x obtained from an "equivalent" nonfilter cigarette, and Wf(x) is the weight of component x obtained from the filter cigarette.

The selective filtration coefficient (Sx) was calculated as follows (10) :

$$Sx=(100-E_{TPM})/(100-Ex)$$

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The results of a detailed comparison of the paired distributions carried out using a CHI^2 test are included in table 2. In line 1, we observe that the distribution of shred size for the Control is indistinguishable from those of R1 and R2c. It must be pointed out that the distribution of shred size for the R1 blend has significantly different distribution of shred size from any other blend (line 2). Because the distribution of sizes for the R1 blend has the lowest average, we can conclude that this type of reconstituted tobacco has a greater brittleness than the other two.

The addition of our experimental sauce to the reconstituted tobacco of the R2 blend caused the distribution to shift to the left (line 3). In other words, an increase in concentration of humectant in the blend caused the blend R2 to be more brittle. On the other hand, the distribution of sizes for RP-RPc (line 4) shifted towards a larger shred despite the presence of 1.5% more propylglycol in RPc than RP.

Figure 2a shows the distributions for the concentration of some anions in the various fractions. In the control blend, phosphates are not uniformly distributed; higher concentrations were discovered in the fractions containing a greater shred size. This may be because phosphates are present in tobacco in 2 forms. At the same time, our aqueous extraction method is not completely efficient if compared to mineralization (6).

Blend R1 stands out because neither phosphates nor nitrates show a uniform distribution. The phosphates have a very narrow distribution with the mode in mesh 6 (0.5 mm) of nominal size, as found in the shred sizes. The distribution of phosphate and nitrates confirm the results found in the size distributions for the R1 blend.

Figure 2b shows the distributions for humectants. The R1, R2, and RP blends contain increasing concentrations of propylglicol and glycerine according to shred sizes.

Propylglycol is more uniformly distributed in the RPc and the R2c blends to which the synthetic sauce was added. Originally the RPc blend contained no propylglycol. These results indicate that a surface activity exists for the adsorption of these compounds, and only in the case of saturation of the active centers can a uniform distribution of humectant be obtained.

Unlike the results found in the blends not made with sauces, the increases found in propylglycol, benzylalcohol and nitrate are uniformly distributed in R2c and RPc. This leads us to believe that the quantities added saturated the active centers of the surface of this type of reconstituted tobacco.

DISCUSSION

If we postulate that the shred has a prismatic shape, the apparent surface of each fraction can be demonstrated as follows:

$$Si = (1+1/n+1/k)*2wi/pt \qquad [1]$$

In the same way, the basal surface of the shred is:

$$Sbi = 2wi/pt \qquad [2]$$

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QUALITY ANALYSIS OF GERMAN TOBACCO CULTIVARS

P. RANGE

SUMMARY

Seventeen German cultivars were analysed according to nitrogen fertilization. New breeding lines as well as common types from cigar, Burley and Virgin types were investigated for smoke and leaf constituents: condensate, nicotine, CO, and NO in smoke; nitrate, alkaloids, sugar, and nitrogen in leaf. The limitation to 12 mg condensate per cigarette, asked by the EEC commission for 1995, can only be fulfilled with the lower stalk positions of the cultivars. Nicotine is changing according to the tobacco types. CO was found in a middle range equal for all types. NO changes according to the nitrogen fertilization and the cultivars. The leaf constituents nitrate, nicotine and the sum of nornicotine and myosmine correlate with cultivar, climate and fertilization.

INTRODUCTION

In 1995 the EEC commission demands the limitation of condensate to 12 mg per cigarette. Further on only tobaccos with a tar content beneath 12 mg per cigarette will be supported. Today most of the produced tobaccos do not fulfill this demand. Only the lower stalk positions of the cultivars show a tar content below 12 mg per cigarette. This is the case for German cultivars.

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EVALUATION OF TOBACCO GRADING SYSTEMS BY MULTIVARIATE ANALYSIS OF THEIR CHEMICAL QUALITY PARAMETERS

EVALUATION DES SYSTEMES DE CLASSIFICATION DE TABACS PAR L'ANALYSE MULTIVARIEE DE LEURS PARAMETRES DE QUALITE CHIMIQUE

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SUMMARY

Three multivariate techniques were considered to evaluate different types and grades of tobacco using the results of nine chemical quality parameters.

Samples of tobacco already graded according to conventional criteria were submitted to a discriminant analysis to evaluate the operativity of the grading systems. Through Mahalanobis distances an order of similarity between types and grades was deduced, thus enabling the search of compatible tobaccos with similar chemical properties. By principal component analysis the system of nine variables was reduced to three components, in such a way, the result of the discriminant analysis was reproduced at 94%. A data file from different kinds of tobacco was analyzed through a non-hierarchical cluster method, which proved the great capacity of this technique to gather objects of similar chemical nature in homogeneous groups, and its advantage in the development of better grading criteria.

The application of these techniques involving physical and organoleptical parameters in addition to the chemical ones, will provide a powerful tool for future studies in this field.

RESUME

On a employé trois techniques multivariantes pour évaluer les différents types et degrés de tabacs en utilisant les résultats de neuf paramètres chimiques de qualité.

En partant d'échantillons classifiés au préalable selon des critères physiques conventionnels, on a fait usage d'une analyse discriminante pour évaluer l'opérativité des systèmes de classification. En utilisant les distances de Mahalanobis, on a pu déduire l'ordre de similarité entre les divers types et degrés permettant la recherche de tabacs compatibles selon leurs propriétés chimiques. En partant des composantes principales, le système de neuf variables a pu être réduit a trois variables, ainsi, les résultats de l'analyse discriminatoire ont été reproduits à 94%. Une méthode cluster non hiérarchique a été appliquée à plusieurs échantillons de différentes classes de tabacs ayant des propriétés chimiques similaires. Cette technique s'est montrée d'un grand potentiel pour le développement de meilleurs critères de classification.

L'application de ces méthodes, qui incluent des paramètres organoleptiques et physiques en plus des paramètres chimiques, pourrait devenir un outil puissant pour des recherches postérieures.

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RESULTS AND DISCUSSION

From the results of our investigations, presented in Tables 1 - 4, it is evident that:

1. The concentration levels of Se for common Burley, Prilep and Virginia tobaccos from different localities or geographical regions are rather similar. The small residual differences are probably due to differences in soil characteristics and genetic factors.
2. In cultivated Istrian Burley, treated with selenium via the soil or by foliar spray, the results show accelerated vegetation and growth, reflected in a lush green mass, in greater branching of roots, in a higher stalk and a larger number of leaves and their dimensions, in early blooming and a larger crop, etc. Further, differences in concentration levels of selenium between bottom, middle and upper leaves and their veins is also evident. In the case of higher concentration levels of added selenium from foliar application, no signs of phytotoxicity were observed.
3. The transfer of selenium from cigarettes prepared from Burley tobacco or from a standard tobacco mixture into main stream smoke and further into crude condensate depends on the design of cigarette, i.e. on the filtration capacity of the filter butts and on the porosity of the cigarette paper.

Concerning the clear phenomenon of the stimulative effects of selenium on tobacco growth, this element can be added by soil supplementation, especially in deficient areas, in the form of various fertilizers.

The accuracy of results obtained was checked by the analysis of different SRMs (Table 2) and good agreement was obtained. This proved the reliability of the radiochemical separation procedure for determination of Se in biological materials developed previously in our department. In the same way, analysis of shredded noncertified reference 2 RI Kentucky Tobacco was performed and the results obtained show a somewhat higher standard deviation, probably because of sample inhomogeneity.

LITERATURE

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several days after manufacture. This is due to excess menthol at or near the surface of the filter fibers eluting into the smokestream. On the other hand, cigarettes A and B, where all menthol was applied to the tobacco, exhibit a slight increase in delivery during the first few days. A reasonable hypothesis for this behavior is that menthol initially in the tobacco that is lost to sidestream smoke migrates to the filter, where it is available to mainstream smoke via elution. In all cases, the menthol distributes between filter and tobacco in a very short time (<20 days) and menthol delivery for all cigarettes becomes nearly indistinguishable.

Note that sample C, to which 25% of the total menthol was applied to the filter, exhibits very little initial slope. This could have significance in terms of minimizing changes in menthol impact immediately after cigarette making.

Figure 4 describes the net gain or loss of filter menthol as a result of smoking. This corresponds to the deposition of menthol onto the filter via the particulate matter, less elution of both absorbed and deposited menthol from the filter during smoking. The equilibrium value is consistently around 0.2 mg of menthol.

Figure 5 demonstrates menthol utilization, which is defined as the percentage of menthol delivered relative to that applied during cigarette manufacture. As expected, utilization decreases over time due to irreversible absorption of menthol into the cellulose acetate filter.

The second part of this study examined the individual contributions of the filter tips and the tobacco columns to menthol behavior. At appropriate intervals, tips were removed from the mentholated cigarettes and smoked on non-mentholated columns (Case I). Similarly, the columns of the mentholated cigarettes were harvested and smoked on non-mentholated filter tips (Case II).

This "mix and match" approach resulted in several interesting observations. Figure 6 shows the menthol delivery from the Case I samples. After equilibration, all cigarettes deliver approximately 0.2 mg menthol, which is only available via elution from the filter. There is a downward trend over time, which is in direct contrast to the upward trend in tip menthol over time (Figure 1). Diffusion of menthol into the bulk polymer of the fibers over time evidently renders the dissolved menthol inaccessible to the smokestream. The decrease in menthol transfer due to depleted tobacco menthol results in a decrease in the excess surface menthol on the fiber, and a decrease in delivery.

Conversely, menthol delivery from the Case II samples exhibits a steady state sometime after day 76 (Figure 7). Menthol deposition onto the non-mentholated filter is also relatively constant after this date. This is understandable in view of the fact that, unlike elution of menthol from the filter, distillation of menthol from the tobacco is complete.

It is interesting to note that if the independent deliveries for a given filter tip/tobacco column are combined (Figure 8), the plots obtained are indistinguishable from those of the original cigarettes (Figure 3). It can be concluded that either: 1) there is no interaction between filter tip menthol content and menthol delivery from tobacco smoke, or; 2) the two are exactly offsetting due to a complex interaction between menthol elution and particulate matter deposition. The latter seems unlikely, although additional experiments are necessary to rule it out altogether.

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CONCLUSIONS

The concentration of anion phosphate is very high in a certain type of reconstituted tobacco, and can be considered as a good tracer for the presence of it in a cigarette blend.

The addition of different types of reconstituted tobacco to a natural blend of tobacco produces a change in the distribution of the shred sizes, and should be taken into account when considering the total weight of tobacco per cigarette.

The distribution of shred size is also influenced by the quantity of sauce added, because the brittleness of the shred is dependent on the surface adsorption of sauce, a fact to be considered when a blend containing a sauce is created.

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Table 3: Selenium content in Burley tobacco (sort B 21), treated with SeO_2 by foliar application, from locality of Sosici, 1988 (µg/g dry weight)

Leaf position	+ 3 mg Se/plant	+ 9 mg Se/plant	+ 42 mg Se/plant	+ 116 mg Se/plant
cutters	7.1	17.5	106.0	443.2
leaf	9.2	30.9	169.3	411.8
tips	9.5	20.9	137.3	411.3
x 1-3	8.6 ± 1.3	23.1 ± 6.4	137.6 ± 31.7	422.1 ± 18.3
Kv %	15.2	30.2	23.0	4.3

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Table 2: Selenium content in Virginia, Burley and Oriental tobacco types from different geographical regions, in µg/g dry weight

Tobacco type	Geographical region	Se (µg/g)
VIRGINIA	Virovitica 1 BO	0.030
	Podravska Slatina 2 A	0.035
	Orašje 1 SL/ST	0.062
	Zimbabwe A 13	0.030
	Zimbabwe E 72	0.035
	Zimbabwe HN 34	0.046
	Zimbabwe A 22	0.052
	Zimbabwe A 12	0.073
	$\bar{x}$	0.045
	σ	0.016
	Kv %	35.0
BURLEY	Virovitica 3	0.079
	Zrenjanin 1	0.102
	Paraguai	0.053
	Onašje	0.055
	$\bar{x}$	0.072
	σ	0.023
	Kv %	32.0
ORIENTAL	Pirot - Prilep 1/4	0.079
	Bitola - Prilep 3	0.095
	Strumica - Jaka 3	0.093
	Radovis - Jaka 1/4	0.072
	$\bar{x}$	0.085
	σ	0.011
	Kv %	13.0
NBS SRM 1572 Citrus Leaves	R ± σ	0.027 ± 0.003
	n	4
	c.v.	(0.025)
NBS SRM 1577 A New Bovine Liver	R ± σ	0.690 ± 0.020
	n	4
	c.v.	0.710 ± 0.070
NBS SRM 1568 Rice Flour	R ± σ	0.340 ± 0.010
	n	6
	c.v.	0.400 ± 0.100
Kentucky Tobacco 2 RI	R ± σ	0.083 ± 0.019
	n	6

n = number of determinations

c.v. = certified value

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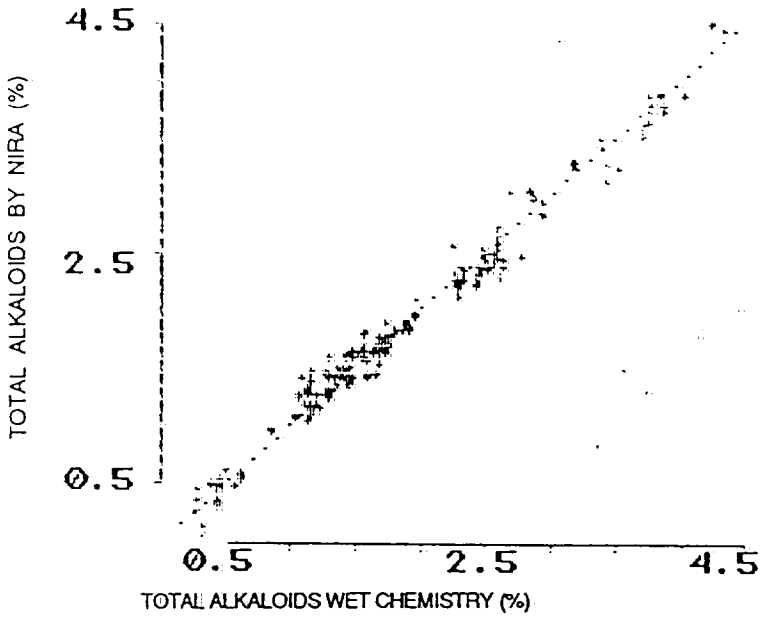
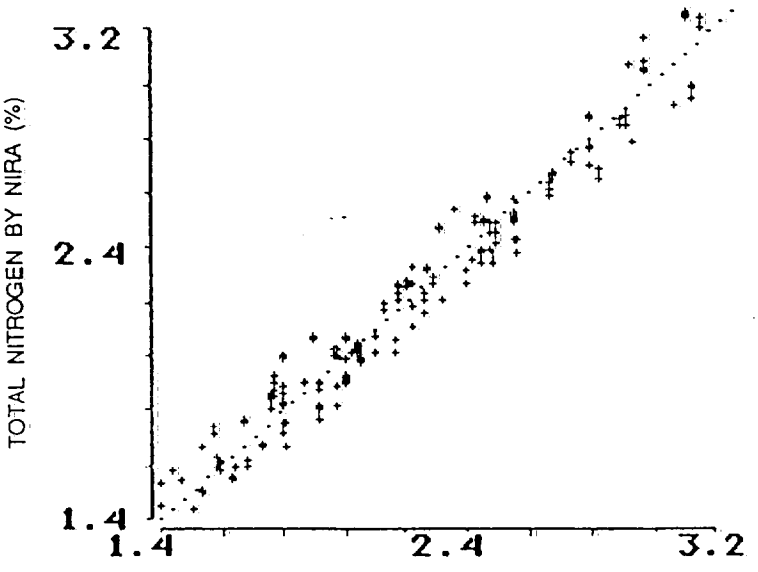
Figures 2 and 3 show the calibration curves obtained by the mathematical processing of data from the first data bank and the equations expressing the dependencies of the spectral changes and the concentrations of total alkaloids and total nitrogen in the tobacco samples.

FIGURE 2
CALIBRATION CURVE FOR TOTAL ALKALOIDS



TOTAL ALKALOIDS (%) = 1.862 + 1.77 (log 1/R)546 - 44.93 (log 1/R)2310 + 220.7 (log 1/R)2270 - 222.0 (log 1/R)2230 + 691.6 (log 1/R)1818 - 512.2 (log 1/R)1759 + 8.614 (log 1/R)1940 - 609.2 (log 1/R)1734 - 34.2 (log 1/R)1722 +807.8 (log 1/R)1680

FIGURE 3
CALIBRATION CURVE FOR TOTAL NITROGEN



TOTAL NITROGEN (%) = 4.941 + 1.677 (log 1/R)546 - 40.64 (log 1/R)2310 - 61.03 (log 1/R)2208 + 118.15 (log 1/R)2180 + 317.96 (log 1/R)1982 - 346.95 (log 1/R)1818 + 805.3 (log 1/R)1778 - 92.66 (log 1/R)1759 + + 13.8 (log 1/R)1940 + 560.32 (log 1/R)1734 - 617.1 (log 1/R)1722 - 34.15 (log 1/R)1445

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TABLE 1

ALKALOIDS, TSNA[a], N-NITROSAMINO ACIDS[a], NITRATE-N, AND NITRITE-N IN CIGARETTE TOBACCO

Compounds	A 24/1.5	B 17/1.1	C 8/0.6	D[b] 7.6/0.03	E 1/0.1	F 1/0.1
Alkaloids (mg/g)						
nicotine	17.9	16.9	17.9	0.4	17.6	17.9
nornicotine	0.7	1.0	0.8	0.6	0.8	0.9
anatabine	1.5	1.5	1.4	1.3	1.7	2.0
anabasine	0.09	0.08	0.08	0.06	0.09	0.11
total	20.2	19.5	20.3	2.4	20.3	20.9
TSNA (ug/g)						
NAT	0.92	1.32	1.46	0.88	1.08	0.97
NAB	0.04	NDc	ND	0.06	ND	ND
NNN	1.29	1.95	2.30	0.88	1.75	1.98
NNK	0.77	0.89	0.53	0.65	0.50	0.58
total	3.0	4.1	4.3	2.5	3.3	3.5
Nitrosamino acids (ug/g)						
NMPA	0.21	0.58	0.38	0.36	0.32	0.52
NMBA	0.006	0.030	0.009	0.040	0.012	0.011
NPRO	0.18	0.64	0.43	0.56	0.28	0.46
Iso-NNAC	0.010	0.026	0.026	ND	0.024	0.028
total	0.41	1.28	0.84	0.96	0.64	1.02
Nitrogen (ug/g)						
nitrate	2,680	2,370	2,780	1,100	3,160	3,080
nitrite	2.65	2.58	2.51	3.97	3.36	3.48
pH	5.32	5.49	5.49	5.38	5.43	5.34

a Abbreviations: TSNA, tobacco-specific N-nitrosamines; NAT, N'-nitrosoanatabine; NAB, N'-nitrosoanabasine; NNN, N'-nitrosonornicotine; NNK, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone; NMPA, 3-(methylnitrosamino)propionic acid; NMBA, 4-(methylnitrosamino)butyric acid; NPRO, N-nitrosoproline; iso-NNAC, 4-(methylnitrosamino)-4-(3-pyridyl)butyric acid.

b Alkaloid, TSNA, and nitrosamino acid values are the averages of 6 samples. One of the samples contained higher concentrations of NAT and NNN (1.38 and 3.31 ug/g, respectively).

c ND, not detected

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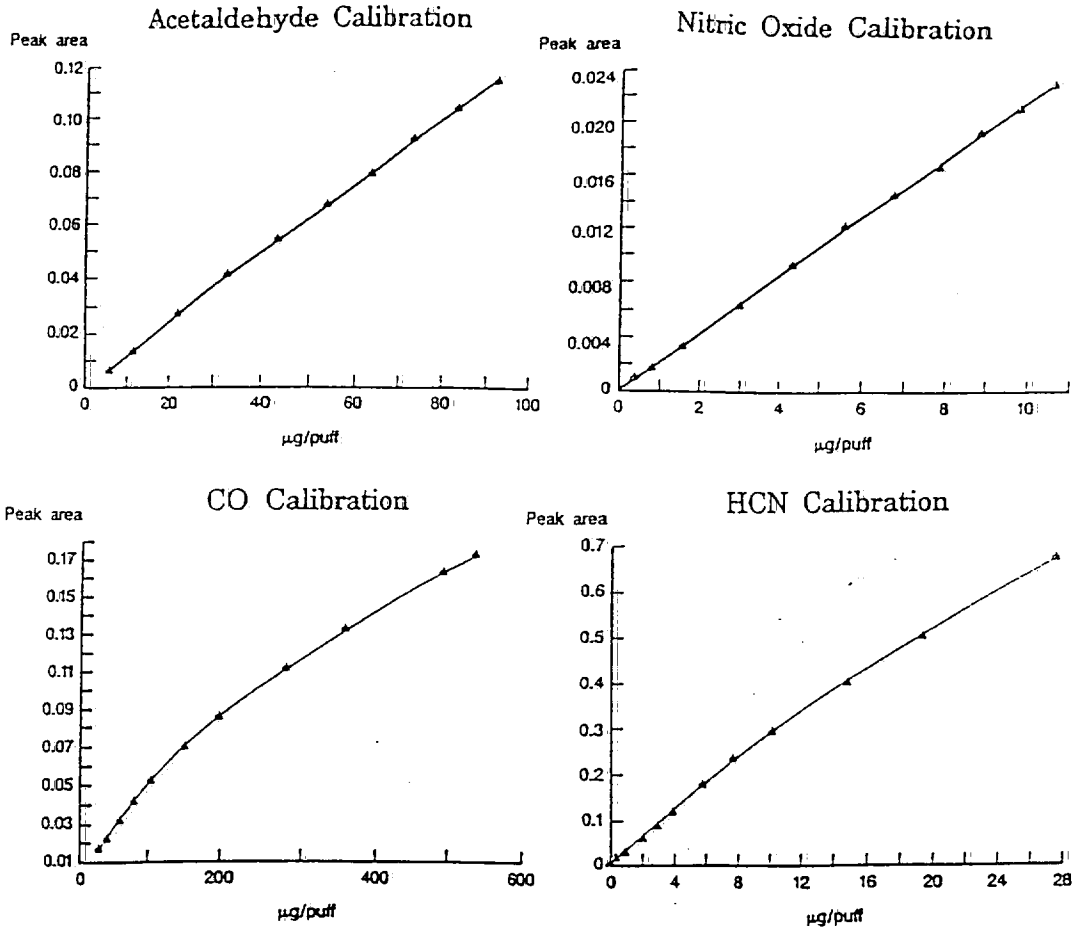

Figure 4: Concentrations of the reference gases are given in µg/puff. The smoke samples were diluted by a factor of ca. 7. Therefore, the effective concentration range, as applied to the smoke samples, is 7 times the values shown. The symbols represent experimental data. Three values are shown for each concentration. The solid line is the calibration curve derived from the experimental data. Acetaldehyde: Linear fit, m = 1.29e-3, b = 0, for concentration = m*peak area + b. Area of integration: 2738 to 2729.5 cm^{-1}, with a baseline drawn from 2766 to 2715 cm^{-1}. NO: Linear fit, m = 2.17e-3, b = 0. Areas of integration: 1904.6 to 1901.8 cm^{-1}, same values used for baseline; 1901.7 to 1898.7 cm^{-1}, sample values used for baseline; 1855.0 to 1851.8 cm^{-1}, same values used for baseline. HCN: Second order polynomial fit: concentration = $17.5x^2 + 28.9x + 0.02$, x = peak area. Area of integration: 716.7 to 710.4 cm^{-1}, same values used for baseline. CO: Second order polynomial fit: concentration = $9987x^2 + 1328x + 4.93$. Area of integration: 2141.1 to 2137.5 cm^{-1}.

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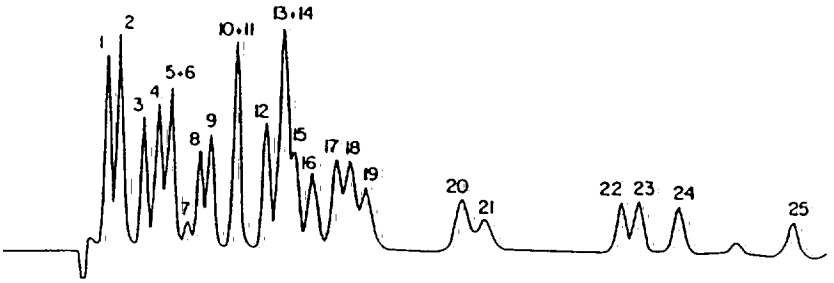

Fig. 1 - CHROMATOGRAM OF A STANDARD MIXTURE OF CARBOHYDRATES SEPARATED BY ISOCRATIC ELUTION. THE NUMBERS OF THE PEAKS CORRESPOND TO THE COMPOUNDS REPORTED IN TABLE I.

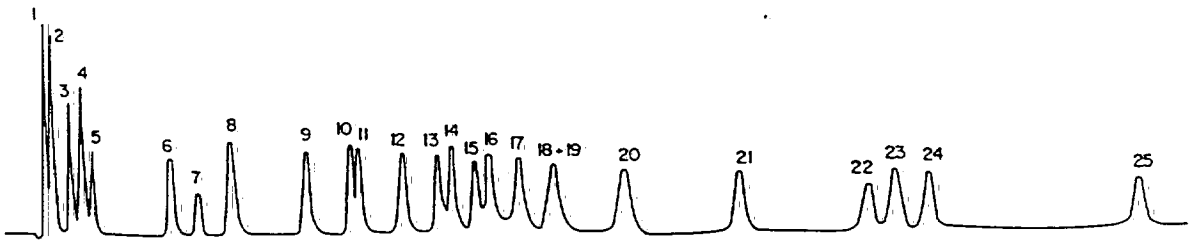

Fig. 2 - CHROMATOGRAM OF A STANDARD MIXTURE OF CARBOHYDRATES SEPARATED BY GRADIENT ELUTION. THE NUMBERS OF THE PEAKS CORRESPOND TO THE COMPOUNDS REPORTED IN TABLE I.

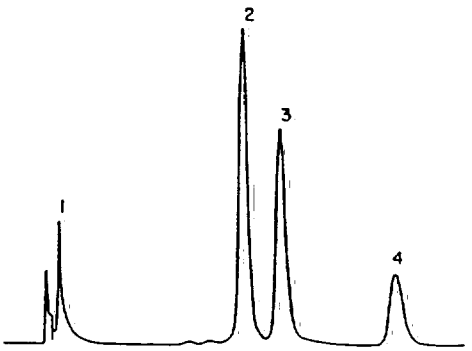

Fig. 3 - BRIGHT - ISOCRATIC ELUTION. METER SCALE: 10 μA

1: INOSITOL; 2: GLUCOSE;
3: FRUCTOSE; 4: SUCROSE

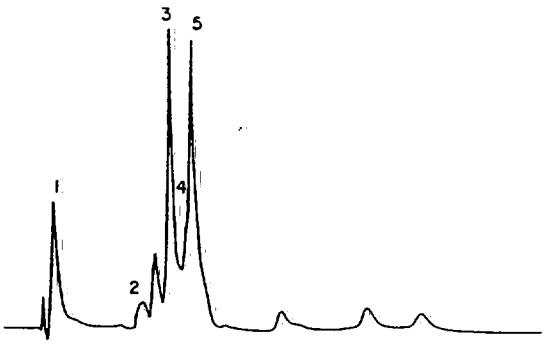

Fig. 4 - XANTY - ISOCRATIC ELUTION. METER SCALE: 10 μA

1: INOSITOL; 2: ARABINOSE; 3: GLUCOSE
4: XYLOSE; 5: FRUCTOSE

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levels in a wide spectrum of food articles, including tobacco, which holds an important position as an article of human consumption. Some research linked to tobacco studies show the physiological effects of selenium on man in areas with higher selenium content in tobacco (Mexico) than in areas of lower selenium content (USA) (3,4).

Hence in the present work some investigations on selenium in tobacco, including observation of the growth and development of tobacco plants (Burley: sort Čulinec and B 21) treated with selenium by soil amendment and foliar application were performed. Further, the determination of the concentration levels of selenium in treated tobacco and in different types of tobacco from various geographical areas was carried out, as well as the selenium content in main stream smoke of some commercial cigarettes or in the smoke of the same type of cigarettes with additional amounts of selenium.

EXPERIMENTAL

Selenium was analysed by destructive neutron activation analysis using radiochemical separations previously developed and checked in our laboratory (5-9).

Irradiation of homogenised (soil) or lyophilised (tobacco) samples and appropriate standards was performed in our TRIGA MARK II REACTOR for about 40 hours in the rotatory specimen rack at a neutron flux of 2×10^{12} $n.cm^{-2}.s^{-1}$.

Briefly, the radiochemical separation of selenium for soil samples is based on pyrolysis in a stream of air and oxygen, volatilization and trapping on soda lime (5). For tobacco the procedure is based on the destruction of the sample with a saturated solution of $Mg(NO_3)_2$, reduction of Se(VI) to Se(IV) with 6 M HCl, and extraction with CCl_4 of the chelate 5-nitro-2,1,3-benzo-selenadiazole resulting from the reaction between Se(IV) and 4-nitro-o-phenylene diamine (6,8,9).

Measurements of the gamma activity of the organic phase for ^{75}Se ($T_{1/2}$= 120 d; E_γ= 0.121; 0.136; 0.264; 0.400 MeV) in samples and standards were performed with a planar or "well type" HP Ge detector, connected to a multichannel analyser.
Chemical yields were shown by tracer experiments to be high (80 - 90 %).

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a N-fertilization of 250 kg per hectare. The cultivar Burlina NA is creating only 0.2 % nicotine together with a high nornicotine content of 1.2 %. The low amounts of the tobacco leaf components are directly correlated with the low amounts of the tobacco smoke contents. These low amounts are due to the tobacco year 1987, a cold and rainy year.

NITROGEN-FERTILIZATION AND NITRIC OXIDE AMOUNTS

A graphic plot of N-fertilization and nitrate contents in tobacco leaves and nitric oxide in tobacco smoke is showing the relationship between high nitrogen-fertilization and the extreme high nitric oxide amounts in tobacco smoke (graph No. 1). All Burley cultivars have been evaluated with the fertilizer concentration 0 kg N per hectare, 180 kg N per hectare and 250 kg N per hectare. The graph is showing clearly increasing rates of nitric oxide in tobacco smoke with an increasing nitrogen fertilization. Without N-fertilization the tobacco plant could only use the soil-nitrogen created during the vegetation period by mineralisation. The nitric oxide content starts at different levels according to the harvesting grades. The curve "leaf" goes from 60 ug NO per cigarette without N-fertilization to 250 mg NO with a N-fertilization of 250 kg per hectare (see graph No. 1, curve "leaf").

In the harvesting grade "tips" 120 ug NO per cigarette without N-fertilization are observed and 320 ug NO per cigarette with 250 kg N-fertilization per hectare (see graph No. 1, curve "tips"). Considering the results, the rates of N-fertilization are in good correspondence with the rates of nitric oxide. Appropriate to the harvesting grade there is a linear proportionality to be seen.

TOBACCO CULTIVARS AND NITRIC OXIDE

A summary of the oxide rates found shows that they usually range in accordance to N-fertilization of the cultivars. It has been found that the Geudertheimer cultivar with a N-fertilization of 180 kg per hectare has a very low nitric oxide range.

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3-Vinylpyridine was present in all sites sampled amounting up to 35 $\mu g/m^3$. Since 3-vinylpyridine is a combustion product of nicotine, it is a useful marker for ETS. In a recent study where nonsmokers were exposed to ETS from high yield and low yield cigarettes, it was found that 3-vinylpyridine correlates very well with urinary cotinine (r=0.98; 15). We did not expect a significant difference in 3-vinylpyridine levels between high yield and low yield cigarettes because the sidestream smoke yields as such are not very different among different cigarettes (16).

The analaytical method reported here using the cryogenic GC-MSD-SIM is very specific and highly sensitive (detection limit $<0.2\ \mu g/m^3$ or <0.3 ng/sample) and should also be suitable for the determination of trace components in other complex matrices.

ACKNOWLEDGEMENTS

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PUFF-BY-PUFF DETERMINATION OF GAS PHASE ACETALDEHYDE, HCN, NO AND CO USING FT-IR SPECTROMETRY.

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SUMMARY

A multi-component, quantitative FT-IR spectrometric method has been developed for the simultaneous determination of the concentrations of acetaldehyde, HCN, NO, and CO present in gas-phase cigarette smoke. A 50 mL portion of gas-phase cigarette smoke from a five-port-smoking machine is trapped in a sample loop, diluted with nitrogen, and transferred to a simple transmission gas cell positioned in the sample compartment of a table-top FT-IR spectrometer. Thirty seconds of the standard one minute smoking cycle are used to collect an infrared spectrum. The remainder of the time period between puffs is used to flush the gas cell with nitrogen. The infrared spectrum contains absorption lines specific for each of the analyte gases. Calibration curves were obtained by relating selected absorption peak areas to known concentrations of the individual gases. The spectral response of an FT-IR spectrometer is stable and frequent calibration is not required. The wavelength accuracy of an FT-IR spectrometer permits automated and reproducible measurement of absorption peak areas. A micro-computer is used to control the flow of smoke and purge gas through the gas cell, and to analyze the spectral data. The entire analytical procedure is designed for simple and reliable operation. The FT-IR spectrometer replaces and provides comparable results to individual instruments currently used for the analysis of each gaseous component.

INTRODUCTION

An FT-IR spectroscopic technique has been developed for the simultaneous, quantitative determination of acetaldehyde, hydrogen cyanide, nitric oxide, and carbon monoxide in gas-phase mainstream (MS) cigarette smoke. Puff-by-puff concentrations for each of the gases were determined by fitting the peak areas of selected absorption lines, present in the MS smoke spectrum, to calibration data. Calibration curves were established by flowing a series of concentrations of reference gases through the sample compartment of the FT-IR spectrometer.

This new method replaces a system that utilized a separate analysis procedure for each gas: a non-dispersive infrared spectrophotometer for CO; an oxides of nitrogen analyzer that detects the chemiluminescence of the reaction product of NO and ozone; and a water scrubbing tower for the entrapment of HCN and acetaldehyde prior to their subsequent colorimetric determinations by an AutoAnalyzer™ procedure. Each of these methods requires daily calibration. The focus in the development of this new analysis procedure was to design a system that is accurate, reliable,

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bought at test markets in CT, FL, OH and NE. All cigarettes were stored in a cold room (4°C) until analysis. Cigarette tobacco was freeze-dried and ground prior to analysis for alkaloids, TSNA, N-nitrosamino acids, nitrate and nitrite, and determination of pH using earlier published methods (7). Standardized procedures for generating and collecting MS were followed (8) except that puff volumes varied. Water in TPM was determined by gas chromatography (9) while nicotine, including secondary amine alkaloids, and TSNA in the MS were assessed as described earlier (7). Benzo(a)pyrene (BaP) was determined by a modified version (10) of the method of Dumont et al. (11).

Apparatus

TSNA were separated and quantified on a Hewlett-Packard Model 5890 gas chromatograph interfaced with a Model 610 Thermal Energy Analyzer (TEA; Thermo Electron Corp., Waltham, MA), modified as described earlier (12), and a Model 3390A integrator (Hewlett-Packard, Paramus, NJ). Tobacco alkaloids were analyzed on a Hewlett-Packard Model 5890 gas chromatograph with a thermionic N-P-specific detector (NPD). Water in TPM was determined on a Hewlett-Packard Model 5700A gas chromatograph with thermal conductivity detector (TCD). MS for TSNA determination was generated with a Borgwaldt RM 20/CS 20-port smoking machine with rotating head (Heinrich Borgwaldt, Hamburg, FRG, modified as described previously; 13). The total particulate matter (TPM) of the mainstream smoke was collected on 92-mm Cambridge filters (CF) as described earlier (7). For determination of water, alkaloids, and BaP in MS cigarettes were smoked in a single-port piston-type smoking machine Model RM1 (Heinrich Borgwaldt, Hamburg, FRG). Nitrate and nitrite analysis was done with a Technicon Auto Analyzer System II with a 50-nm flow cell in the colorimeter (14). BaP analysis was carried out by reverse phase HPLC on a Hewlett Packard liquid chromatograph Model HP 1090 interfaced with a Hewlett-Packard fluorescence detector Model HP 1046A.

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METHODS, MATERIALS AND INSTRUMENTS

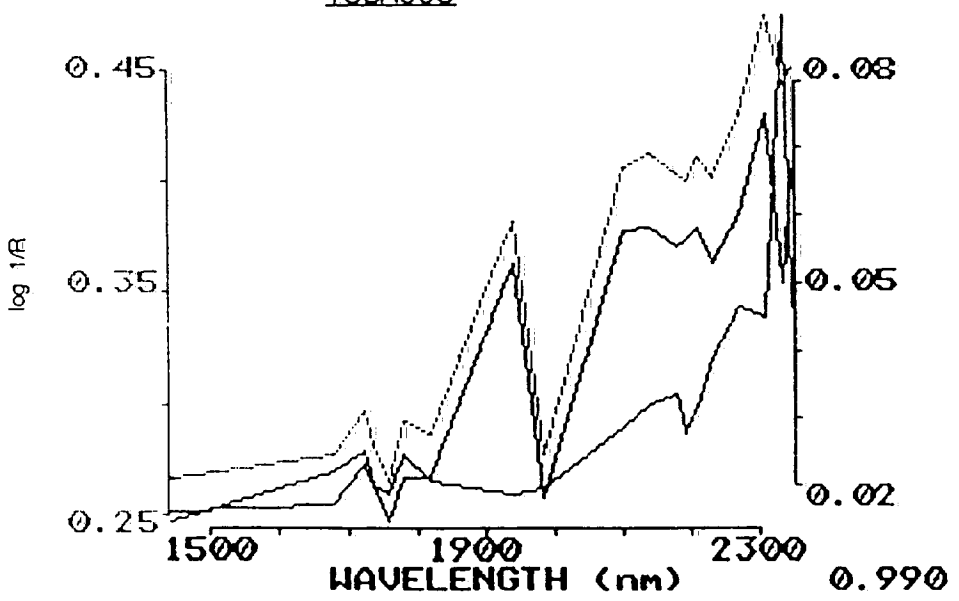
A TECHNICON INFRAALYZER 450 R + computerized filter spectrophotometer was connected to an IBM XT PC computer. All chemical and spectral data were stored in the computer's memory.
A PERKIN ELMER 139 UV/VIS spectrophotometer was used to determine the total alkaloids after distillation in an alkaline medium (CORESTA Standard Method No. 20). Digestion according to KJELDAHL on a TECATOR DS 20 system was used to determine the total nitrogen content. A total of 180 tobacco samples were selected from the material received at the chemical laboratory of the Tobacco institute Zagreb. The samples were selected with reference to the tobacco type (flue-cured) and with reference to the total nitrogen content (1.2-4.0%) and the total alkaloids (1.0-4.5%).

The samples were dried to a moisture content of 3-4% and ground on a WILLEY mill through an 0.2mm sieve. The optical parameter was log 10 (1/R) and was obtained by scanning through 19 filters according to the order of the firm TECHNICON called the "tobacco combination". All the samples were placed in a cuvette by the same operator to achieve the greatest possible uniformity. Each sample was scanned at least twice, and the analyses by classical methods were also repeated. The spectra (19 points) obtained by NIR and results of the classical chemical methods on 120 tobacco samples were stored in the computer data bank which were used to determine the calibration curves. The data for remaining 60 samples were used to check the calibration curves obtained. Step-wise multiple regression was used to select the appropriate wavelengths , and the ratio between the residual values and the residual standard deviation were used to eliminate inappropriate sample spectra.

RESULTS AND DISCUSSION

By plotting the spectral data and the wavelengths, spectra similar to the usual absorption spectra were obtained with peaks distributed in accordance with absorbing compound. Figure 1 shows the spectra of two samples with different chemical composition. In these two samples the difference in the content of total alkaloids was about 0.8 %, and in the content of total nitrogen about 0.5 %.

FIGURE 1
SPECTRAL DIFFERENCES FOR TWO SAMPLES OF FLUE CURED TOBACCO



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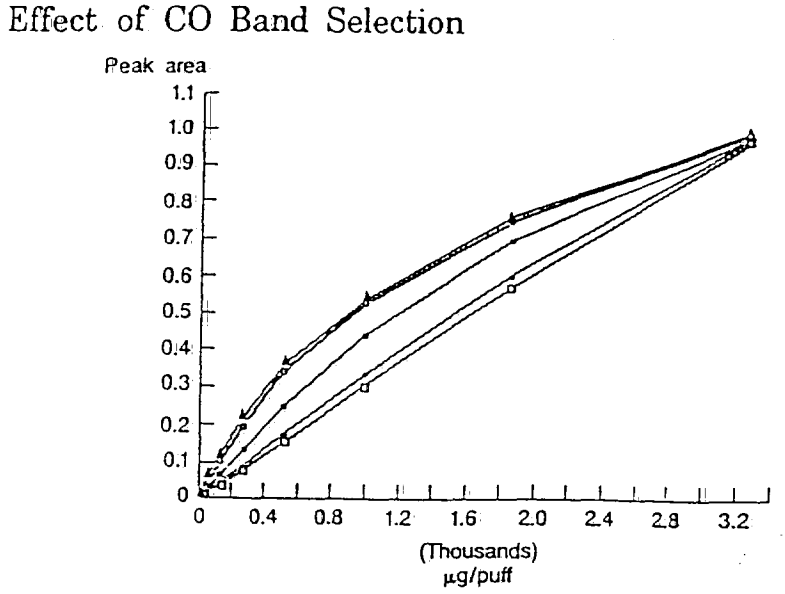

Figure 3: All peak areas are normalized to the peak area of the most concentrated sample. □: peak 2230.3 cm^{-1} ; •: peak 2221.5 cm^{-1} ; ■: peak 2203.3 cm^{-1} ; °: peak 2193.3 cm^{-1} ; Δ: peak 2176.2 cm^{-1} . A spectrum of carbon monoxide is shown in Figure 5.

between the peak areas of CO and HCN and concentration are non-linear. A second-order polynomial fit of the data is used to determine the levels of CO and HCN. The small CO absorption lines that vary linearly with concentration were not used. They appear in regions of smoke spectrum that overlaps with CO_2 or carbonyl sulfide.

The HCN peak is adjacent to a CO_2 peak. The concentration of CO_2 in smoke is high and the CO_2 peak slightly overlaps the HCN peak (Figure 5d). To eliminate this interference, a scaled subtraction of a reference spectrum of CO_2 is made from the sample spectrum. The scaling factor is determined by the ratio of CO_2 sample peak height to that of the reference spectrum. The wavelength accuracy of FT-IR spectrometers, based on the wavelength of an internal helium-neon laser, allows for accurate subtraction of spectra. This wavelength accuracy also assures that the peak areas of the analyte gases can be reproducibly determined automatically from computer stored wavelengths.

Table I lists the results from the analysis of 2R1F, 2R1, and 1R4F Kentucky reference cigarettes by both the FT-IR and established procedures. The two analysis techniques demonstrated excellent agreement for CO and NO. These gases were determined by direct gas phase analysis by both systems. The comparison was not as good for HCN, and acetaldehyde. The FT-IR procedure uses direct gas-phase analysis for these components, whereas the established procedure uses an AutoAnalyzer procedure following extraction in a water tower. The differences in values for the latter gases may be attributed to the uncertainties introduced by water extraction and chemical complexation prior to analysis utilized in the established

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OPERATING CONDITIONS
Temperature: room-temperature in the range 18-23°C;
PAD operating parameters: E_1=0.10V ; E_2=0.60V; E_3=-0.80V
$T_1=T_2=T_3$=300msec;
Meter scale: 10KnA;
Chart speed: 1.0cm/min;

For isocratic elutions:
Flow rate: 0.6ml/min;
Eluent: NaOH 0.1N or H_2O(65%)+NaOH 0.2N(35%);

For gradient elutions:
Flow rate: 1.0ml/min;
Gradient program:

TIME (min)	WATER (%)	NaOH(0.2N) (%)
0	100	0
5	100	0
8	85	15
16	85	15
46	10	90
50	10	90
51	100	0

Post column reagent: NaOH 1N at flow rate of 1ml/min.

RESULTS

Carbohydrates behave as weak acids with a pKa in the range 12-14. They are present in the anionic form in solutions with a pH>12 and can be retained and separated on anion exchange columns. Carbohydrates are also easily oxidized on the surface of noble metal electrode such as gold. For these reasons the anion exchange chromatography with pulsed amperometric detection represents a choice method providing many advantages, as specificity, selectivity and sensivity(6).
The pulsed amperometric detector uses a multistep potential wave form of three different voltages, each applied for a few hundreds of milliseconds, resulting in alternating anodic and cathodic polarizations. The first positive voltage allows, through an oxidating reaction, the amperometric detection of the $-CH_2OH$ functions of carbohydrates; the second higher positive potential cleans electrochemically the electrode surface, while the third negative voltage reduces gold oxide back to gold.
With such a detector only molecules having oxidable functional groups can be detected and therefore only compounds with amino or sulfide groups can interfere, while carboxylic acids and

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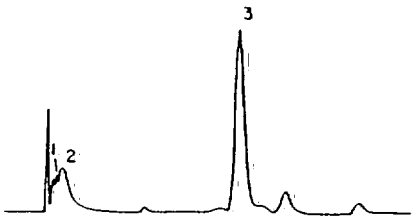

Fig. 5 - BURLEY - ISOCRATIC ELUTION. METER SCALE: 10 μA
1: INOSITOL; 2: XYLITOL; 3: GALACTOSE

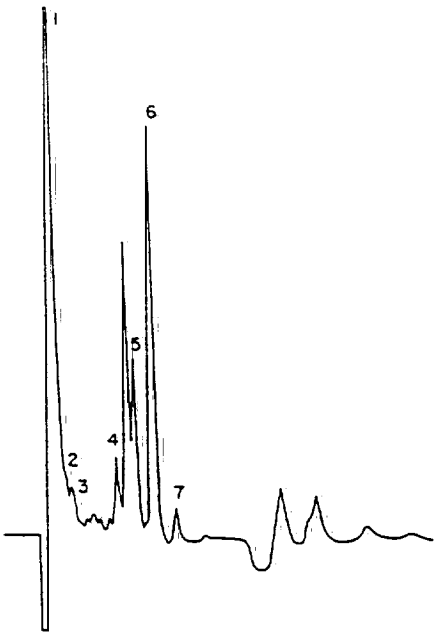

Fig. 6 - MARYLAND - ISOCRATIC ELUTION. METER SCALE: 3 μA
1: INOSITOL; 2: TREHALOSE; 3: 2-DEOXY-D-RIBOSE;
4: ARABINOSE; 5: GLUCOSE; 6: FRUCTOSE; 7: MELIBIOSE

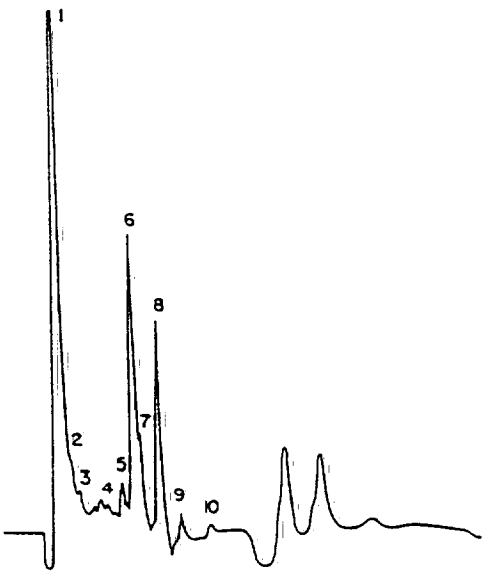

Fig. 7 - KENTUCKY - ISOCRATIC ELUTION. METER SCALE: 3 μA
1: INOSITOL; 2: SORBITOL; 3: MANNITOL; 4: RAMNOSE;
5: ARABINOSE; 6: GLUCOSE; 7: XYLOSE; 8: FRUCTOSE;
9: MELIBIOSE; 10: SUCROSE

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ing agent in tobacco and tobacco smoke (8), several studies have concentrated on the analysis of only nicotine in ETS (9-12). Among the most common analytical methods used are trapping of nicotine on Cambridge filters treated with potassium bisulfate (4,10,13), trapping of nicotine on XAD resins (5,9,13) or trapping of whole ETS on Tenax tubes with subsequent analysis by thermal desorption followed by gas chromtography (GC; 11) or mass spectrometry (MS; 12). In a recent study, we have analyzed several volatile ETS components such as 1,3-butadiene and benzene using GC-MSD (14). It was the goal of this study to analyze in detail selected volatile and semivolatile ETS components using thermal desorption-GC-MSD.

MATERIALS AND METHODS

Apparatus. The GC-MSD system consisted of a Hewlett Packard Model 5890 gas chromatograph interfaced with a Model 5970 MSD, an HP 59970 GC-MS workstation software run on an HP 9000 series 300 computer. The gas chromatograph was equipped with a Chrompack thermal desorption cold trap injector (# 16230) and a cryogenic control for liquid CO_2. The sampling of ETS was carried out using a portable vacuum pump (DuPont Alpha 1).

Analysis of ETS. Air samples were collected on glass cartridges packed with 200 mg Tenax TA (20-35 mesh) preconditioned at 250°C overnight. A total of 1.5 l air per sample was collected at a flow rate of 50 ml/min (under these conditions, no breakthrough was observed).

The sample cartridges were desorbed at 250°C for 10 min. using a cryotrap at -73°C which subsequently was heated to 250°C at 15°/sec. The gas chromatographic column was a 30 m x 0.25 mm (i.d.) DB-5 (1 micron film thickness) fused silica. The GC oven was kept at -20°C for 2 min. and then ramped to 250°C at 20°C/min. The injection port temperature was kept at 250°C and the carrier gas had a flow rate of 1 ml He/min. The MSD was operated in the SIM mode at four different time "windows". Under these conditions, the entire chromatogram eluted in 17 minutes (Figure 1).

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low-cost, and automated. Recent advances in FT-IR spectrometer instrumentation has made available low-cost, rugged, low-maintenance systems well suited for reliable analytical laboratory applications. The FT-IR spectrometer is equipped with a maintenance-free, room-temperature, deuterated triglycine sulfate (DTGS) detector, and simple transmission gas cell with replaceable, low-cost KCl windows. An interface delivers the smoke from the smoking machine to the FT-IR spectrometer and purges the sample cell between puffs. The entire analysis procedure, with the exception of the lighting of the cigarettes is automated.

ANALYSIS SYSTEM DESIGN

Cigarettes were smoked on a five-port smoking machine using a 35-mL, 2-second duration puff, every 60 seconds. Cigarettes were smoked to a butt length of 3 mm from the tipping paper for filtered cigarettes. The environmental smoking conditions of temperature and relative humidity were maintained at 24 ° C and 60% relative humidity. The smoke passes through a standard Cambridge filter pad (0.3 micron pore size) in a Lucite® filter assembly. The 175 mL output of the smoking machine is pushed through a sample loop connected to the interface of the smoking machine and FT-IR spectrometer (Figure 1). The opposite end of the sample loop is open to an atmospheric pressure vent. After a short delay period of 2 seconds, the sample loop is connected to the analysis loop. The analysis loop consists of the sample loop, a peristaltic pump, and the gas cell in the sample compartment of the FT-IR spectrometer. The pump is activated and the smoke sample, diluted with nitrogen, circulates through the analysis loop for 35 seconds. The sample spectrum is obtained during this time. The analysis loop is purged with high pressure nitrogen during the last 20 seconds of the one minute smoking cycle. The timing of the smoking cycle, pump activation, sample-scan period, and valve operation is controlled by a programmable controller. The FT-IR spectrometer computer communicates with the smoking machine programmable controller and analyzes the data at the end of the smoking cycle.

The analysis sequence is initiated by the operator entering the program name. A spectrum is then obtained of the nitrogen purged sample cell. This spectrum is used as a background for the sample spectra. Experimental effects of factors such as variation in source intensity, contamination of the gas cell windows, or misalignment of the gas cell are eliminated by dividing sample spectra with a background spectrum acquired immediately prior to the analysis. A report is generated at the end of the analysis detailing the puff-count for each port of the smoking machine, the concentrations of each of the analytes per puff, and a total concentration for each cigarette. Sample names are entered into the program by a bar-code reader. The FT-IR computer is interfaced to a mainframe computer where analysis data are stored.

A Laser Precision Analytical RFX-30 series 2 cm^{-1} FT-IR spectrometer is used. The spectrometer is controlled by an IBM PC/AT compatible computer. An important feature of the spectrometer is its permanently-aligned, refractively scanned interferometer with mechanical bearings. An air-cooled source is used.

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8. NIST SRMs Catalog 1990-91, Mc. Kenzie Ed., NIST Spec. Publ. 260, Washington, 51-53.

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Table 1: Results for selenium (µg/g dry weight) in soil and in untreated as well as SeO_2 treated Burley (sort Čulinec and B 21) tobacco, cultivated at Valtinjana and Sosici

	Valtinjana 1, sort Čulinec				Sosici, sort B 21	
	1984		1985		1988	
Soil: depth 20 cm	0.27		0.16		2.9	
depth 30 cm	1.10		0.84		3.2	
Position of tobacco leaves	control (untreated)	+ 5 mg Se/plant	control (untreated)	+ 5 mg Se/plant	control (untreated)	+ 20 mg Se/plant
sundy	0.230 ± 0.012	0.600 ± 0.020	0.233 ± 0.018	0.620 ± 0.024	0.554 ± 0.018	3.10 ± 0.17
cutters	0.124 ± 0.015	0.303 ± 0.020	0.170 ± 0.019	0.358 ± 0.025	0.440 ± 0.020	2.10 ± 0.19
leaf	0.074 ± 0.018	0.273 ± 0.015	0.075 ± 0.015	0.281 ± 0.096	0.245 ± 0.019	2.40 ± 0.15
tips	0.072 ± 0.011	0.163 ± 0.012	0.062 ± 0.011	0.179 ± 0.018	0.284 ± 0.022	1.90 ± 0.10
stem	0.035 ± 0.010	0.102 ± 0.011	0.046 ± 0.011	0.095 ± 0.015	0.090 ± 0.020	1.30 ± 0.12
$\bar{x}$ 1-5	0.106 ± 0.076	0.288 ± 0.192	0.117 ± 0.081	0.307 ± 0.202	0.360 ± 0.100	2.16 ± 0.66
Kv %	71.7	66.8	69.0	65.7	54.0	31.0

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SELENIUM CONTENTS IN TOBACCO AND MAINSTREAM CIGARETTE SMOKE

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SUMMARY

In the domain of essential trace elements the role of selenium is extremely important. As one of the volatile elements it can be partly absorbed through the pulmonary system during smoking and transported to different organs of the body. From this point of view a knowledge of its concentration levels in various sorts of tobacco and in the smoke of commercial cigarettes, as well as in the same type of cigarettes from plants treated with selenium is of interest for various research fields.

The purpose of this contribution is to present reliable quantitative data on contents in tobacco, soil and main stream cigarettes smoke, obtained by destructive neutron activation analysis.

INTRODUCTION

Microelements have vital roles in physiological processes in all living organisms. Among them in the last thirty years selenium is attracting more and more interest. As an essential element selenium induces a series of favourable effects, including functions such as direct influence on vitamin C synthesis, substitution for vitamin E, as well as antagonistic effects towards toxic heavy metals and an important role as constituent part of the enzyme glutathione peroxidase which catalyses the destruction of peroxides in organisms (1) For efficient functioning of selenium in living organisms, concentration levels of 0.04 - 0.1 ppm in the diet are necessary; on the other hand, with excess quantities of this element toxic effects can result (2). Accordingly, in many biomedical and environmental research areas the increasing awareness of the role of trace selenium in human and animal health has stimulated interest in investigation of its concentration

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ANALYSIS OF SELECTED ENVIRONMENTAL TOBACCO SMOKE COMPONENTS IN INDOOR AIR BY THERMAL DESORPTION-GC-MS

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SUMMARY

In recent years, environmental tobacco smoke (ETS) has been the subject of increased research activities. In order to measure the concentration of selected ETS components in indoor air, we developed a sensitive analytical method which utilizes a portable vacuum pump in conjunction with a Tenax trap, a thermal desorption injection device and gas chromatography-mass selective detection (MSD). The latter was operated in the selective ion monitoring mode (SIM) to optimize selectivity.

Compounds analyzed include benzene and alkylbenzenes, pyridine, picolines, 3-vinylpyridine, limonene and nicotine. We sampled several smoking and nonsmoking environments (restaurants, bars, cars, homes, offices etc.).

Nicotine was found at levels ranging from 0 to 117 µg per m^3, while the concentration of the other volatile organics ranged from <0.1 to 167 µg/m^3. Limonene was found at very high levels in a restaurant and a new car (254-320 µg/m^3), possibly due to the use of some lemon-scented cleaning agents.

The system is very sensitive, allowing the analysis of only 1.5 l air (detection limit <0.3 ng of nicotine per sample). In addition to nicotine, 3-vinylpyridine was found to be a good marker for ETS exposure.

INTRODUCTION

Environmental tobacco smoke (ETS) has been recognized as an important component of indoor air pollution. Recent epidemiological studies have incriminated ETS as a risk factor for lung cancer in nonsmokers (1-3). As a result, several studies have been undertaken to analyze ETS (4-7). Since nicotine is the habituat-

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EXPERIMENTAL SET UP

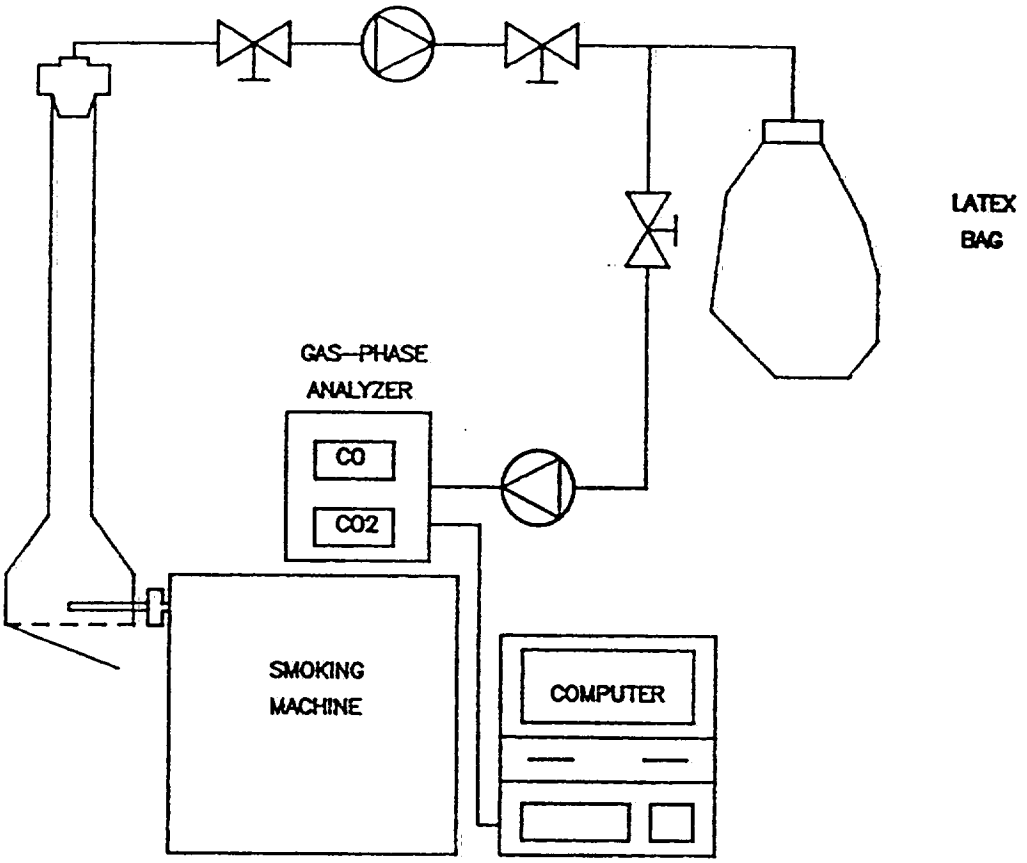

Figure 1

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

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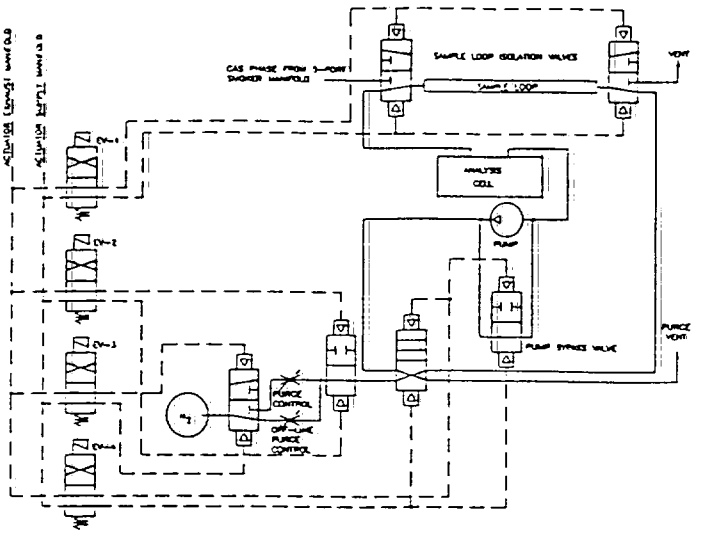

Figure 1: Valve EV-1 when actuated supplies air to drive the sample isolation valves, opening the sample loop to the discharge of the 5-port smoker's exhaust. Valve EV-2 turns the nitrogen supply off when actuated. Valve EV-3 routes the nitrogen supply through a large throttling valve when actuated, supplying a high volumetric flow rate through the sample loop and analysis cell during on-line purging. When deactuated, it routes the nitrogen supply through a small throttling valve to provide a constant low volume purge during system down periods. Valve EV-4 closes the sample-analysis loop when actuated, and closes the pump by-pass valve. When deactuated, it allows the desired purge flow of nitrogen to flow through the sample-analysis loop, bypassing the pump.

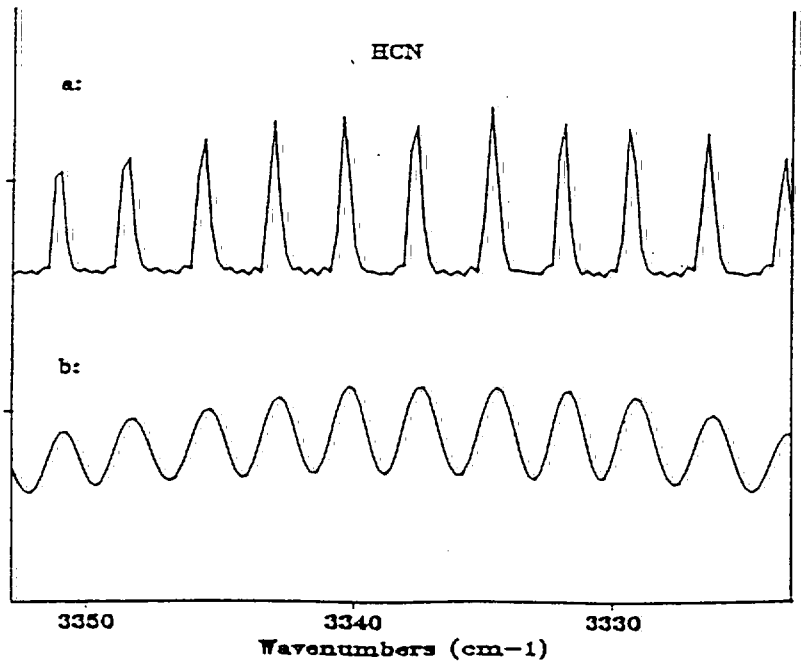

Figure 2: a: Spectrum of HCN acquired at 0.5 cm^{-1} resolution. b: Spectrum of HCN acquired at 2 cm^{-1} resolution.

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

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tight 18 m^3 stainless steel room have been described previously (4) and a comprehensive paper will be published. After smoking various numbers of cigarettes in the chamber (MS is exhausted), the air concentrations and their decays were monitored. When deriving yields per cigarette, data were extrapolated back to the middle of the smoking to compensate for decays.

Smoking sessions in an office

The office used for this study is located in a modern building with central air conditioning. It is mechanically ventilated, with 3 louvers on one wall near the perforated ceiling. It is meant for occupancy by 2 people, with a volume of 49.3 m^3. The walls are plastered and the floor carpetted. It is furnished, with 2 facing desks standing together in the center of the room. In all experiments, air mixing was assured by 2 fans located at opposite corners of the room. Smoking was performed by a smoking machine laying on a corner of one of the desks or by 2 smokers sitting at that corner. Smokers were trained to take 2-sec puffs every minute, with volumes close to 35 ml. It was verified that puff counts were virtually the same for both smokings. Sampling was performed as close as possible to where someone's head would be if he were sitting at the other desk. In some sessions, the door was partially open, while in others louvers were partially plugged.
Two types of smoke generation were performed: Pulses, where ETS decay is monitored after 2 to 4 cigarettes are smoked, and continuous generation where cigarettes are smoked at regular intervals (3-6 cig./h). In that case a steady state was reached after about 2 hours.

ETS monitoring

The procedures used for ETS monitoring are the same as those previously described (9). Aerosol particulate matter (APM) was monitored using a piezobalance (discrete measurements every 6 min.) and by filter gravimetry according to (15) (integrated over 30 min.) as a cross check on the above.

RESULTS AND DISCUSSION

Theoretical modelling of ETS concentrations

To assist in the interpretation of experimental studies on ETS performed in mechanically ventilated offices, many models have been proposed (10-12). In the present study we use a single-compartment model i.e. assume that the concentrations are uniform in the room. The release of smoke components is supposed constant during smoking and all sink rates taken as first order.

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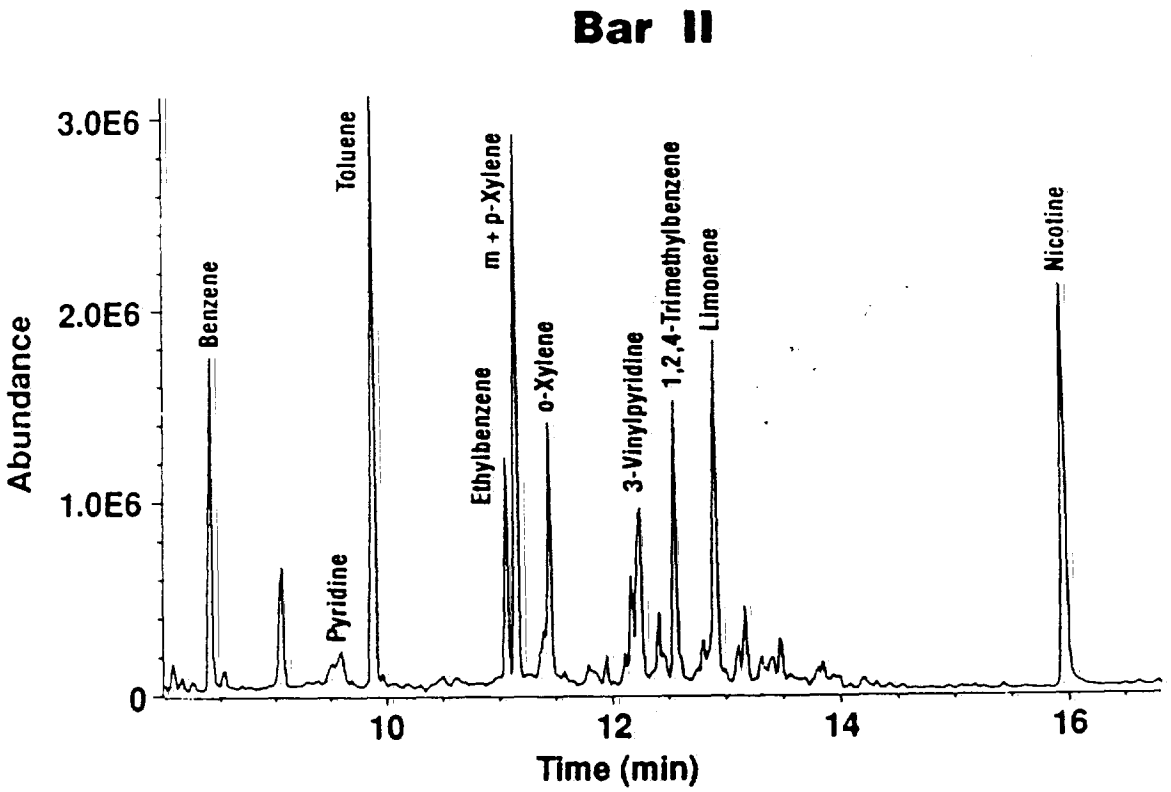

Figure 1. Gas chromatogram of selected components in ETS.

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TABLEAU 2

INFLUENCE COMPLEXE DES FACTEURS ETUDIES
SUR LA COMPOSITION DE LA FUMEE

TRAITEMENTS	COMPOSITION DE LA FUMÉE, MG/CIG.					
	TÉMOIN I			TÉMOIN II		
	GOUDRONS	NICOTINE	CO	GOUDRONS	NICOTINE	CO
No.1357	31,00	1,43	21,99	-	-	-
No.2468	25,21	1,27	15,20	-	-	-
RÉDUCTION/CIG.	5,79	0,16	6,79	-	-	-
POURCENT	18,67	11,19	30,88	-	-	-
No.1357	31,00	1,43	21,99	-	-	-
No.2469	24,06	1,28	18,81	-	-	-
RÉDUCTION/CIG.	6,94	0,13	3,18	-	-	-
POURCENT	22,58	9,10	14,46	-	-	-
No.2357	-	-	-	27,91	1,37	20,72
No.2468	-	-	-	25,21	1,27	15,20
RÉDUCTION/CIG.	-	-	-	2,70	0,10	5,52
POURCENT	-	-	-	9,67	7,30	26,64
No.2357	-	-	-	27,91	1,37	20,72
No.2469	-	-	-	24,06	1,28	18,81
RÉDUCTION/CIG.	-	-	-	3,85	0,09	1,91
POURCENT	-	-	-	13,79	6,56	9,22

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effect upon senses from effects of other numerous components), permanent changes of the conditions governing the formation of smoke and eventually individual interpretation by degustators. Most of the authors agree that the physiological strength of smoke depends directly upon the nicotine content in tobacco (consequently in smoke with known transfer conditions). The reports on nicotine's role in other sensory qualities vary. Some authors (7, 9, 10, 11) state that it has definite negative correlation with quality; others (1) indicate significant positive correlation (especially with taste strength) and some have not found a consistent relationship (2, 15, 16).

Considering water solubility of nicotine and the fact that primary sensory effects are formed in the oral cavity we have tried to find the role which nicotine dissolved in saliva can have in organoleptic properties. Keeping in mind pharmacology and the organoleptic characteristics of the pure substance we supposed that the primary effect would be demonstrated by strength and off-effects (irritation - biting in throat).

EXPERIMENTAL

A one-year study with commercial cigarettes, taken by free choice, from all quality groups of Yugoslavian cigarettes was conducted. We have paid attention to examine all cigarette brands of our market. This made up a sample of 4320 cigarettes.

All tested cigarettes were conditioned for one week at 21°C and 60% relative humidity and selected on a weight and pressure drop basis. The cigarettes were smoked on the smoking machine RM-20 Heinr. Borgwaldt by the standard method of CORESTA.

Tubes with CSC were rinsed continuously with saliva imitation at 36°C with liquid flow rates according to the mean puff flow rate. Further fraction separation was done by the method of Snook (12).

The samples of the neutral fraction were analysed on Varian 3400 gas chromatograph equipped with capillary column DB-1. The

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most of the inorganic species do not. The molecules containing carbonyl functions are not oxidized at the operating conditions followed in the present work(7,8).
Furthermore the anion exchange chromatography allows a good separation of a large number of carbohydrates, from monosaccharides to low molecular-weight polysaccharides, while non-ionic and basic compounds, even if oxidizable, are not retained and elute in the void volume without any interference.
It is still possible to get a high sensitivity: amounts in the range 1-50ng are easily detected (table 1). In the gradient elutions the sensitivity is increased adding a more concentrated solution of sodium hydroxide (1.0N) at the end of the separator column, keeping relatively constant, in this way, the pH in the detector cell and achieving also the lower drift of the baseline. It must still be pointed out that carbohydrate degradation in high pH solutions has not been observed since these reactions are slow on the time scale of chromatography.
The chromatographic parameters of 25 carbohydrates are given in table 2. The retention times and the values of k' were obtained under isocratic conditions. The retention times under gradient conditions are relative to rhamnose.
Twenty-two out of twenty-five carbohydrates were separated and identified by isocratic elution and twenty-four out of twenty-five by gradient elution. The chromatograms are shown respectively in Figures 1 and 2.

TABLE 1
DETECTION LIMITS FOR SOME SUGARS IN TOBACCO

SUGARS	DETECTION LIMITS (ng)	SUGARS	DETECTION LIMITS (ng)
Inositol	1.0	Xylitol	15.0
Glucose	4.0	Sucrose	50.0
Fructose	4.0	Arabinose	15.0
Galactose	5.0	Melibiose	25.0
Xylose	2.5		

ANALYSES OF TOBACCO

The tobacco leaves or the cigarette filler were ground and amounts of mg 100 of tobacco powder were weighed. The samples were shaken twice with 50ml of distilled and purified water and both extracts were combined and filtered. The solution was then injected through an ON-GUARD RP filter into the sample injection valve of the chromatograph using a 50µl sample loop, not later than eight hours after the extraction, because the solutions of carbohydrates extracted from tobacco were not stable even at low temperature.

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injection temperature was 250°C, the detector temperature was 300°C and the oven temperature was programmed from 50°C to 250°C at 15°C/min. The carrier gas, helium, was maintained with flow rate of 3 ml/min. Identification of the nicotine maximum was done on Finnigan MAT 8230 mass spectrograph under the same working conditions (Fig. 1 - the example of GC and MS identification).

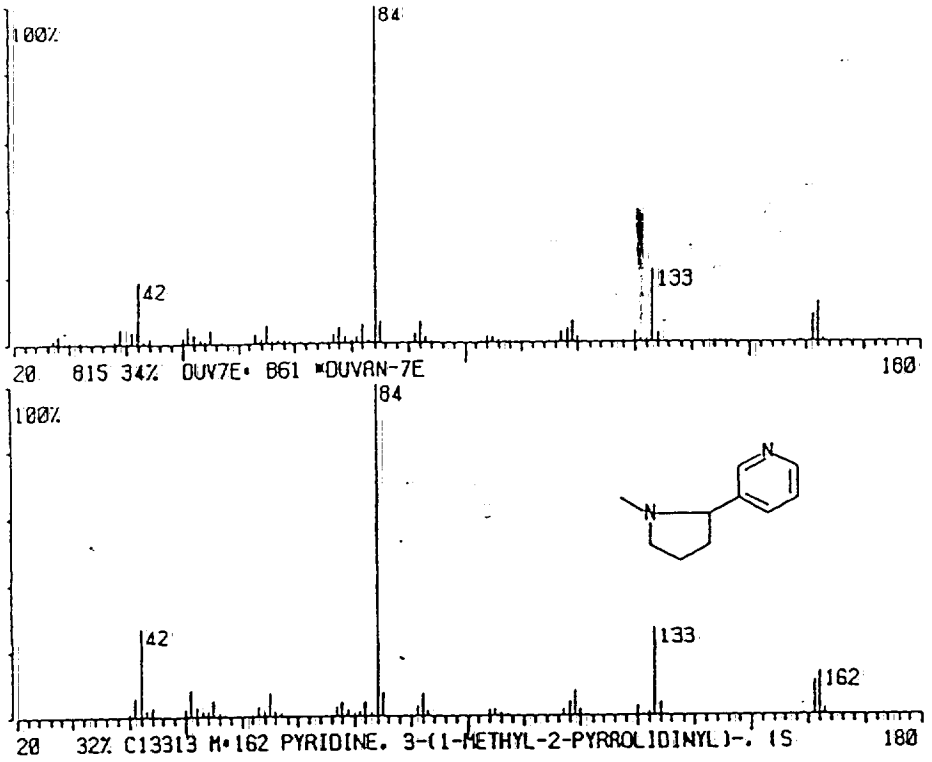

Fig. 1: The gas chromatogram obtained from neutral fraction of one cigarette of 3rd quality group

Degustation of cigarettes was carried out by an internal degustation system of the degustation board from the tobacco factory of NAIS. This system allots an equal number of points (1-10) for each sensory quality in three categories - very, medium and little. Descriptive estimation follows each number of given points.

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QUANTITIES OF ARSENIC AND ANTIMONY IN TOBACCO AND SMOKING CONDENSATE

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SUMMARY

Tobacco, like other plants, contains varying amounts of trace elements, depending on the soil composition, the specification of the elements, and on the characteristic absorptive properties of the plant. In tobacco, arsenic and antimony are sometimes found in higher concentrations.

During smoking volatile arsenic and antimony can be transferred from tobacco to cigarette smoke. Hence for studies and research on the transfer of these two elements by different sorts of tobacco, reliable data on the concentration levels of arsenic and antimony in soil, tobacco leaves, and cigarette smoke are of importance.

Arsenic and antimony were analysed by destructive neutron activation analysis (NAA) using rapid radiochemical separation based on extraction of their iodides. The accuracy of the results obtained was checked by the analysis of Standard Reference Materials (SRMs) and good agreement with certified values was obtained.

INTRODUCTION

In all living organisms and their processes minute quantities of some elements can play a significant biological role (1). Soil, climatic conditions, fertilizers, different agricultural sprays and the characteristic absorptive properties of the plant can influence the concentration levels of essential or toxic inorganic constituents in plant materials. Among them, tobacco holds a leading position as an article of human consumption and is one of the most frequently used plant in the study of mineral composition and nutrition (2).

Investigations of the arsenic content in tobacco has a long history, but for antimony data are very scarce. Until recently both elements were

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TABLE 1

SELECTED COMPOUNDS IN ENVIRONMENTAL TOBACCO SMOKE ($\mu g/m^3$)

Compound	Restaurant		Bar	Car		Office	Home		Lab	Garage
	NS	S	S	NS	S	NS	NS	S	NS	NS
Benzene	36	69	107	40	31	15	9	47	5	29
Pyridine	4	n.d.	16	n.d.	0.6	0.4	n.d.	3	0.2	0.4
Toluene	62	26	167	7	42	30	68	134	15	121
2-Picoline	1	5	7	1	n.d.	0.3	n.d.	n.d.	n.d.	0.1
3 + 4-Picoline	2	8	13	1	1	0.6	1	1.5	n.d.	0.4
Ethylbenzene	10	21	44	72	9	4	36	13	3	40
m + p-Xylene	19	43	131	o.l.	36	12	119	48	8	134
o-Xylene	11	22	52	104	12	5	45	19	3	57
3-Vinylpyridine	2	18	35	17	2.5	1.4	10	10	0.6	5.3
1,2,4-Trimethylbenzene	17	61	55	38	13	6	56	21	6	72
Limonene	254	320	94	292	17	10	5	27	n.d.	2
Nicotine	6	103	117	2	14	3.7	n.d.	17	n.d.	n.d.

NS = nonsmoking; S = smoking; n.d. = not detected (<0.2 $\mu g/m^3$); o.l. = overload.

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INFLUENCE OF SMOKE DILUTION AND ENVIRONMENTAL CONDITIONS ON THE MEASURED LEVELS OF ETS COMPONENTS.

EFFET DE LA DILUTION ET DES FACTEURS D'ENVIRONNEMENT SUR LES CONCENTRATIONS OBSERVEES DE CERTAINS COMPOSES DE LA FUMEE AMBIANTE.

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Research & Development, Philip Morris Europe, Neuchatel, Switzerland

SUMMARY

Cigarette emission yields have often been used to compute ETS exposures in indoor environments, but this approach rests on many assumptions and experimental results in this domain vary widely.
In this study, the sidestream smoke (SS) emission yields of 2 experimental cigarettes with different filter ventilations were measured in a first step using a single-cigarette total-recovery device.The SS from these cigarettes was also released into a 18 m^3 air-tight chamber, and the resulting air concentrations were measured. Eventually, the cigarettes were smoked in an office of a modern, air-conditioned building. Both human smoking and the release of SS only were studied. Different patterns of smoke generation and various room ventilation rates were tested.
The results from these sets of experiments are compared, and some implications for exposure assessment are discussed.

RESUME

On utilise souvent les rendements d'émission des cigarettes pour estimer l'exposition à la fumée ambiante dans un local. Cette approche repose sur de nombreuses suppositions et les résultats expérimentaux varient considérablement suivant les auteurs.
Dans le présent travail, on a tout d'abord mesuré les rendements émis dans le courant secondaire CS de 2 cigarettes expérimentales ayant des dilutions filtre différentes au moyen d'un collecteur individuel du CS total. Le CS fut également produit à l'intérieur d'une chambre hermétique de 18 m^3 pour mesurer les concentrations résultantes. L'expérience fut enfin répétée dans un bureau à air conditionné d'un immeuble moderne. On y a étudié à la fois le fumage humain et l'émission de CS seulement. On a testé différent taux d'échange d'air et différents profils de génération de fumée.

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Table I: Results for As and Sb in various tobaccos, filter butts, tar and standard reference materials ($\mu g\ kg^{-1}$ dry weight)

Type of tobacco and other samples	Locality	Position of leaves	As	Sb
PRILEP	Bitola (Yu)		550	49
	Pirot (Yu)		590	145
	Radovište (Yu)		540	46
	Strumica (Yu)		430	54
VIRGINIA	Orašje (Yu)		310	58
	Podravska Slatina (Yu)		300	51
	Virovitica (Yu)		130	20
	Zimbabwe		70 - 100	8 - 17
BURLEY	Orašje (Yu)		460	31
	Paraguay		320	22
	Virovitica (Yu)		230	49
	Zrenjanin (Yu)		440	75
ISTRIAN BURLEY	Valtinijana (Yu)	bottom	160	39
sort: Čulinec		middle	410	62
		upper	560	61
untreated		vein	340	31
	soil		17000	690
ISTRIAN BURLEY	Valtinijana (Yu)	bottom	2400	166
sort: Čulinec		middle	420	77
		upper	520	125
treated with As and Se		vein	193	10
ISTRIAN BURLEY	Sosići (Yu)	bottom	5040	80
sort: American B 21		middle	1240	70
		upper	490	99
treated with As and Se		vein	430	20
	soil		20000	680
KENTUCKY TOBACCO 2 RI			505 ± 66 (n = 6)	63 ± 10 (n = 6)
CTA-OTL-1* Oriental Tobacco Leaves			432 ± 75 (n = 4)	45 ± 7 (n = 4)
CTA-VTL-2* Virginia Tobacco Leaves			897 ± 57 (n = 4)	270 ± 45 (n = 4)
Filter butts µg/kg of Burley Tobacco			30 - 70 (n = 8)	9 - 15 (n = 8)
Tar µg/kg of Burley Tobacco			2 - 12 (n = 12)	0.5 - 5 (n = 12)
NBS SRM 1577 A (8) New Bovine Liver			56 ± 3 (n = 6) c.v. 47 ± 6	31 ± 0.1 (n = 5) (30)
NBS SRM 1572 Citrus Leaves			3380 ± 50 (n = 6) c.v. 3100 ± 300	34 ± 1 (n = 6) 40 ± 10

c.v. = certified value
n = number of determinations
* = Candidate reference materials from the Polish Academy of Science, Warsaw.

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Other ETS components

Ammonia and HCN were investigated as representative of reactive gas phase components. For practical reasons NH_3 and HCN could only be quantified in ETS in steady state experiments. Emission yields are derived from equations [1] & [2] with m = 1 and c_d set to its value in the experimental chamber. The results in table 1 show that what was observed for nicotine also takes place for NH_3 but on a smaller scale, whereas it is likely that the model could reliably be used to predict HCN concentrations in ETS.

Human smoking experiments

In fact ETS originates from both SS and exhaled MS (EMS). Some experiments where C20 cigarettes had been machine smoked were duplicated with human smoking, in order to assess the EMS contribution to ETS. On average, it was found to be 19% for CO, 46% for APM and 20% for NOx, in range with (17).

CONCLUSION

The emission yields of the SS of 2 experimental cigarettes were determined under very different environmental conditions and aging:
The fresh smoke was directly sampled using a total collection device. The smoke was also released into a room-size, air-tight chamber. Eventually SS was generated in a mechanically ventilated office and a single-compartment, exponential model was used to interpret these last results.
The fundamental difference between SS and ETS was apparent when comparing the 3 sets of experimental data: due to evaporation, the RSP concentration in ETS is only a fraction of what could be predicted on the basis of SS data. The chamber results are a better but still inadequate approximation. This is even more true for nicotine, due to its fast removal by surfaces and its complex kinetics. These biases are less pronounced but observable for other ETS components. This makes good use of ratios and markers very delicate. Most of all, it makes predictive models of ETS exposure rather unreliable, as was shown for a semi empirical formula aimed at predicting RSP levels on the basis of room parameters, SS yields and smoking rate. Even for "well-behaved" compounds like CO, biases inherent to the use of single compartment models were demonstrated: part of the emitted smoke may be evacuated before it can be distributed in the room by air drafts and diffusion, especially at higher air-change rates. Finally, the experimental cigarettes, which have very different MS yields, were found to have similar SS yields, showing the fallacy of reasoning in terms of SS / MS ratios.

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where wi is the weight of each fraction g
p is the solid density g/cm3
t is the thickness (average) of the shred cm(10)
n is the ratio of width to thickness
k is the ratio of length to thickness

Equations [1] and [2] provide values for the total and basal apparent surfaces for each fraction. They calculate the theoretical value for the surface of a prismatic shred containing no pores or wrinkles. In other words, the equations provide underestimations of the values obtained during adsorption experiments (10), which can be as much as 60 times greater than values calculated with the above equations. However, if we consider the surface wrinkles to be constant and independent of the size of the shred, the calculated values are proportional to the real values.

Assuming the components of the sauce are adsorbed mainly in the basal surface of each shred, similarly to moisture (10), a representation of basal surface versus the total quantity of sauce in each fraction (figure 3) is a straight line whose slope is proportional to the mass of sauce adsorbed per surface unit. The two continuous lines in the figure correspond to the distribution of total sauce for RPc and R2c, and were calculated by adding to the original quantities measured in the R2 and RP blends those quantities that corresponded to the composition of our experimental sauce. It is supposed that adsorption took place only in the basal surface of the strip.

As seen in figure 3, RP has the lowest level of humectant adsorption per surface unit, while R1 shows an intermediate value between that of RP and R2. The graph also indicates that both blends R2c and RPc,showed losses compared to their theoretical values, and the losses were greater (≈63%) in the case of the RPc blend.

Table 3 shows the computed average diameters as computed from the sizes distribution, ans also the index for the total surfaces computed from the equation 1 above.

Table 3. - Average diameters and total surfaces for the different blends.

	Ctrl.	R1	R2	R2c	RP	RPc
Diameter mm	1.379	1.227	1.946	1.283	1.775	2.060
Diameter index	100	89	141	93	128	149
T. surface index	100	101	95	100	98	95

The addition of sauce causes an increase of 5% in the total apparent surface of the R2 blend as a result of the comminution of the shred in the cigarette maker. This process is enhanced by the presence of pores in the surface of the shred, which become filled with humectant and act as tear points. On the other hand, the surface of the RPc blend adsorbs less sauce than R2 therefore causing it to spread within the blend, leading to the adhesion of shreds while lowering the total apparent surface by 3%.

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With these assumptions, and following Leaderer (10) and Repace (11), simple solutions for the mass balance differential equation can be written:

1) At equilibrium for a constant smoking rate of n cigarettes per hour, the air concentration C_{equ} of a smoke component is:

$$C_{equ} = n.E / V.k \quad \ldots [1]$$

where E is the emission per cigarette, V the room volume and k the first order constant for removal of the component. More explicitly:

$$k = m.(c_v + c_d) \quad \ldots [2]$$

where c_v is the mechanical ventilation rate, c_d is the rate of removals due to decay processes and m is a correction factor accounting for mixing dynamics (perfect mixing: m = 1)

2) During smoke concentration build-up, $C_{(t)}$, concentration corrected for the background level (so that $C_{(0)} = 0$) can be written:

$$C_{(t)} = C_{equ} (1 - e^{-kt}) \quad \ldots [3]$$

3) After smoking, when emission ceases as it reaches C_{max} and for t being the time after emission ceased, it becomes:

$$C_{(t)} = C_{max} e^{-kt} \quad \ldots [4]$$

Model testing using carbon monoxide results

Carbon monoxide is a compound for which $c_d = 0$ i.e. $k = m.c_v$ from Equ. [2]. This provides an accurate and simple way of testing the model, using data from pulse experiments with C20 cigarettes. The actual decay rate k is found by fitting the CO data in the decay phase to an exponential (equation [4]). The emission rate E can then be computed - equations [1] & [3] - from data on the smoke build-up and CO concentration peak value. Computed yields are plotted in figure 1 as a function of the decay rate k. They can be compared to those derived from chamber results:

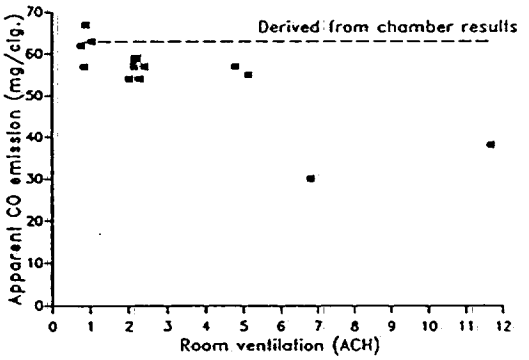

FIGURE 1: Apparent CO emission vs. room ventilation

It appears that the model is very good at low air exchange rates i.e. below 1.5 air change /hour (ACH). Results are 10 to 15 % too low thereafter, and at ACH > 6 they are only about 50% of the actual yield.

The fact that the model calls for emission yields which are lower than the actual yields outlines a bias due to the use of single compartment models: Air mixing becomes less effective as room ventilation is increased. This may result in smoke being cleared before it can be evenly distributed in

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The statistical analyses were done with a programme for multiple correlation on a personal computer PC-12.

RESULTS AND DISCUSSION

The results of CSC separation are summarized (average values) in Table 1.

Quality group	CSC mg/cig.	Nicotine in CSC	Neutral fraction (mg/cig.)	Neutral fraction (% in CSC)	Nicotine in NF (%)
License	19,36	1,34	6,17	31,85	1,o3
Extra q.g.	2o,22	1,41	6,9o	34,12	1,42
1st q.g.	21,4o	1,o2	9,o3	42,17	1,89
2nd q.g.	21,51	1,o7	9,25	42,23	1,73
3rd q.g.	23,51	1,49	12,19	51,85	1,91
4th q.g.	24,17	1,51	13,59	56,24	2,17

Table 1: Parameters of CSC
- middle values for 360 cigarettes
in each quality group

The results indicate that with decreasing quality the content of CSC increases, which was expected. The share of the neutral fraction and nicotine in it increases with decrease in the cigarettes quality too. These differences are particularly important for the percentual share of the neutral fraction for the best and the worst quality - up to 24, 36%. Connecting these findings with the noticed organoleptic properties (Tab. 2), we have found out that if the portion of the neutral fraction exceeds 50% of CSC, the smoke coated tongue gave the impression of "greasity". The sensations of biting and burning are insignificant for the 2nd quality group; middle for 1st and 3rd quality group and are accentuated for the cigarttes of 4th quality group. By the same order the nicotine content in the neutral fraction increases (Tab. 2).

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Quality group	Completness (points)	Correlation coef. r_1	Strength (points)	Correlation coef. r_2
License	7,839	o,78	3,o52	o,69
Extra q.g.	7,631	o,82	6,795	o,71
1st q.g.	7,1o8	o,82	6,7o4	o,68
2nd q.g.	o,891	o,86	6,635	o,66
3rd q.g.	6.542	o,87	6,333	o,61
4th q.g.	6,353	o,89	6,238	o,63

Table 2: Relations between nicotine content in neutral fraction of CSC and some organoleptic properties (average values)

The intensity of these irritating effects violates the fullness of "completeness". The middle values cannot show the real differences. According to them, except license cigarettes, which have full "completeness", all the others can be judged as cigarettes with middle "completeness". However, the statistical analyses of multiple variations give correlation coefficients which explain the nature of relationship (Tab. 2). So we see that dependence of "completeness" on the nicotine content in neutral fraction is high. The degree of dependence is higher for the lower quality groups. This can be explained by the lesser effect and smaller number of other components in the fraction which can have a camouflage effect.

The influence of nicotine in the neutral fraction on strength is of middle range and almost the same within all quality groups. This indicates that, for strength, the nicotine content in the basic fraction is probably more important.

Forming the multiple regression equation for "completeness" (X),

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As was to be expected, there were no changes in the chemical composition of the tobacco blend with sorbitol in comparison to the tobacco blend without sorbitol.

Some characteristics of the experimental cigarettes are presented in Table 2.

TABLE 2
SOME CHARACTERISTICS OF THE EXPERIMENTAL CIGARETTES

SORBITOL %	TOBACCO WEIGHT mg/cig.	DRAW RESISTANCE mm WG	PUFF NUMBER per cigarette
0	800	66	10.2
1	800	66	10.1
3	800	67	10.4
5	800	68	10.5

All the cigarettes contained the same amount of tobacco, had an almost identical draw resistance, and the puff number per cigarette varied slightly.

The tar levels of the cigarettes, the nicotine content in the smoke condensate and the carbon monoxide content in the mainstream smoke of the cigarettes are shown in Table 3.

TABLE 3
TAR, NICOTINE AND CARBON MONOXIDE LEVELS OF THE EXPERIMENTAL CIGARETES

SORBITOL %	TAR mg/cig.	NICOTINE IN SMOKE CONDENSATE mg/cig.	CARBON MONOXIDE mg/cig.
0	22.1	2.15	19
1	21.8	2.12	19
3	21.8	2.13	18
5	22.1	2.12	18

The results presented are the average values of a series of determinations. Regardless of the concentration of sorbitol in the tobacco blend, the tar, nicotine and carbon monoxide yields of the cigarettes were almost identical.

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Source: https://www.industrydocuments.ucsf.edu/docs/xskm0000

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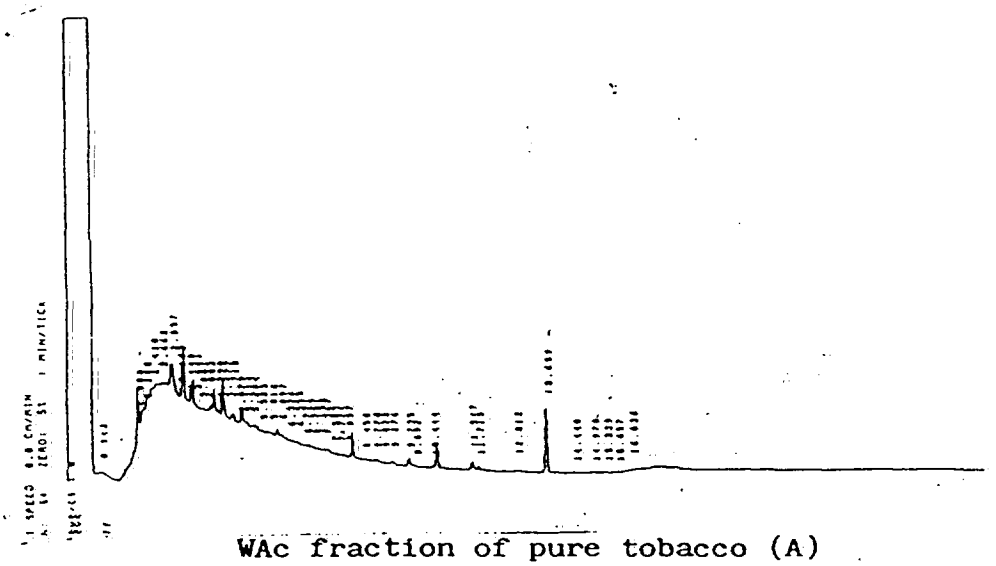
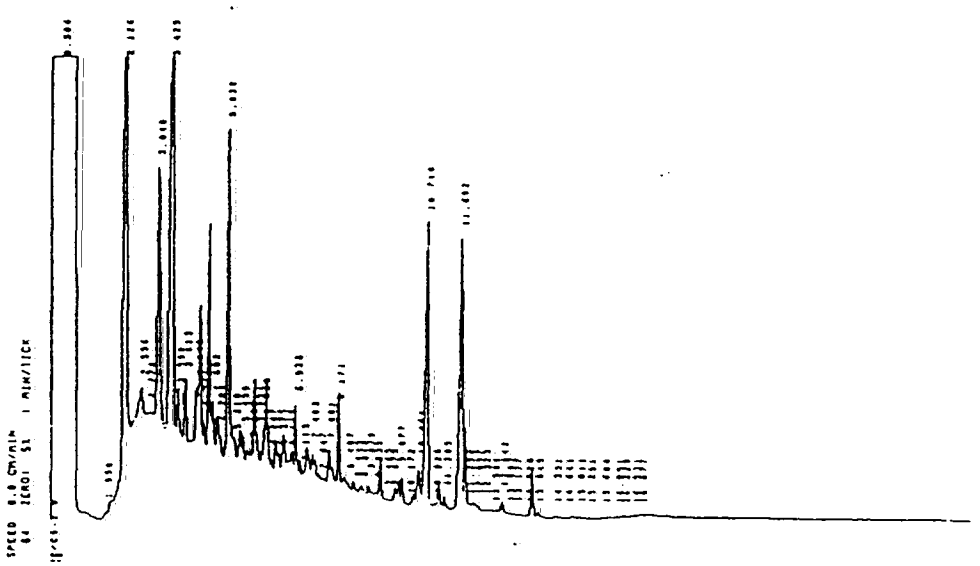
RESULTS AND DISCUSSION

Gas chromatograms of weak acids of Burley tobacco and Burley tobaccos treated with sugars are given in Fig. 2. A-E



WAc fraction of pure tobacco (A)



WAc fraction of tobacco with bonbon syrup (B)

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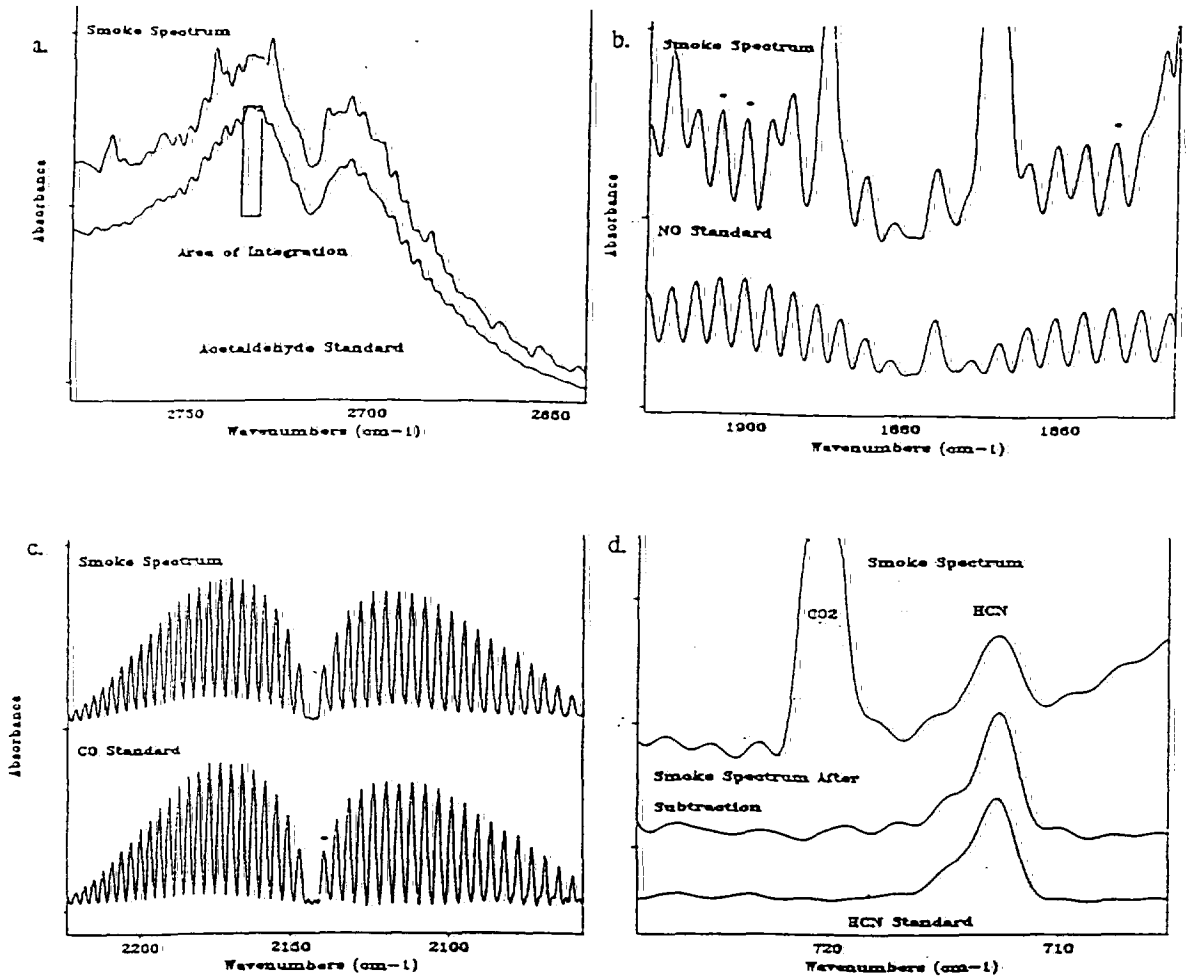

Figure 5: a: Acetaldehyde. The box shows the area integration. b: Nitric oxide. The * indicates the peaks used for analysis. c: Carbon monoxide. The * indicates the peak used for analysis. d: Hydrogen cyanide.

procedure. Reanalysis of the reference cigarettes by the FT-IR method after 10 days produced results within 7% of those listed in Table I.

CONCLUSIONS

The FT-IR method provides a means of using a single instrument system to determine the concentrations of acetaldehyde, HCN, NO and CO in cigarette smoke. FT-IR spectrometers are rugged and require very little maintenance. A strong point in the favor of the FT-IR method is that the analysis of other gases present in smoke could be added in the future by changes in software and collection of appropriate calibration spectra.

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D.P.F. CES MODIFICATIONS DES CIGARETTES N'ENTRAÎNENT PAS DE MODIFICATIONS DES PROPRIÉTÉS DE FUMAGE CARACTÉRISTIQUES AU TYPE ET À LA MARQUE ET PEUVENT, PAR CONSÉQUENT, ÊTRE UTILISÉES AVEC SUCCÈS.

INTRODUCTION

LE PROBLÈME DE RÉDUIRE L'INFLUENCE NOCIVE DE LA FUMÉE DE CIGARETTES SERA TOUJOURS ACTUEL JUSQU'À CE QUE LE CONTENU DES SUBSTANCES DANS LA FUMÉE NE SOIT RÉDUIT AU MINIMUM POSSIBLE. POUR CELA, IL EST NÉCESSAIRE DE SURMONTER LA CONTRADICTION ENTRE UN GOÛT ET UNE ACTION PHYSIOLOGIQUE SUFFISANTE D'UNE PART ET UN NIVEAU BAS DES GOUDRONS ET DE LA NICOTINE D'AUTRE PART (6). EN RÉSULTAT, DES EXIGENCES NORMATIVES POUR LES NIVEAUX DES GOUDRONS ET DE LA NICOTINE DANS LA FUMÉE PEUVENT ÊTRE OFFICIELLEMENT RÉGLEMENTÉES (2,5).

L'ON SAIT QU'UNE RÉDUCTION IMPORTANTE PEUT ÊTRE ATTEINTE SOUS L'ACTION DE TOUT UN ENSEMBLE DE FACTEURS. UNE COMBINAISON PRÉCISE DES FACTEURS MÈNE À UN RÉSULTAT FINAL PRÉCIS (1,3,4). DE PLUS, IL FAUT PRENDRE EN CONSIDÉRATION LE FAIT QUE CE RÉSULTAT N'EST PAS UNE SOMME SIMPLE DES RÉDUCTIONS INDIVIDUELLES SOUS L'EFFET DE CHAQUE FACTEUR. LES INTERDÉPENDANCES SONT TRÈS COMPLEXES ET LE RÉSULTAT FINAL NE PEUT ÊTRE ÉTABLI QUE PAR VOIE EXPÉRIMENTALE (5).

CE TRAVAIL A EU POUR BUT D'ÉTUDIER LES POSSIBILITÉS DE RÉDUIRE LES GOUDRONS, LA NICOTINE ET LE MONOXIDE DE CARBON DANS LA FUMÉE DE CIGARETTES SOUS L'ACTION DE DIFFÉRENTS FACTEURS.

MATÉRIAUX ET MÉTHODES EXPÉRIMENTALES

LES ÉLÉMENTS COMPOSANTS LES COMBINAISONS DES DIFFÉRENTS FACTEURS SONT LES SUIVANTS:

-COMPOSITION DU MÉLANGE: 1. MÉLANGE (CIGARETTE) STANDARD
2. MÉLANGE (CIGARETTE) EXPÉRIMENTAL

- UTILISATION DE CÔTES: 3. CÔTES EXPANSÉES
4. CÔTES NON EXPANSÉES

- ADDITIFS AU TABAC: 5. SANS ADDITIF

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considered as toxic, but new literature data show evidence for the essentiality of As, while for Sb its beneficial or toxic effects for living organisms are still in the phase of extensive investigation (1).

Both elements are included in the group of elements which can be partly volatilized in the smoke and inhaled, and so are of prime interest in studies of pulmonary absorption in man. Thus the purpose of our work is to present reliable quantitative data on concentration levels of As and Sb in different sorts of domestic and foreign tobaccos, filter butts and tar after smoking of an appropriate number of cigarettes with a mechanical smoker. The results were obtained by the use of NAA with a rapid radiochemical separation developed and tested previously in our laboratory (3-6).

EXPERIMENTAL

1. Irradiation: Neutron irradiation of lyophilized samples and appropriate standards was performed in our TRIGA MARK II REACTOR for about 20 hours in the rotatory specimen rack at a neutron flux of 2×10^{12} $n.cm^{-2}.s^{-1}$.

2. Radiochemical separation: Briefly the radiochemical separation is based on wet destruction of the samples (200-300 mg; H_2SO_4 + HNO_3 + H_2O_2), on subsequent extraction of AsI_3 and SbI_3 in toluene and on selective stripping of antimony from the organic phase with a mixture of 6 M HCl/ 0.5 M KI.

3. Measurement of γ-activity: Measurements of the γ-activity of the organic phase for ^{76}As ($T_{1/2}$= 26.4 h; E_γ = 0.559 MeV) and the HCl/KI phase for ^{122}Sb ($T_{1/2}$= 2.7 d; E_γ= 0.560 MeV) were performed with a "3x3" NaI/Tl "well type" detector, or with planar and "well type" HP Ge detectors connected to a multichannel analyser.

4. Chemical yields were shown by tracer experiments to be quantitative.

RESULTS AND DISCUSSION

Arsenic and antimony are volatile elements at high temperature and so can be partly absorbed through the pulmonary system during smoking into blood, liver, lung and especially kidney. Hence knowledge of the concentration

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EXPERIMENTAL

Cigarettes

Burley tobacco, $U_{1/3}$ grade, was sprayed with concentrated aqueous solutions of p.a. fructose (D), glucose (E), saccharose (C) and bonbon syrup (B) up to 25 % of tobacco dry mass. The sprayed tobacco was thermally treated under standard conditions and manufactured into cigarettes (85 mm). The cigarettes were conditioned and selected on the basis of average weight and pressure drop. The control cigarette (A) was sprayed with an equivalent volume of water.

Smoking of cigarettes

The cigarettes were smoked on a H. Borgwaldt smoking machine model RM 20 giving 35± 0,3 ml puff of two-second duration once a minute. Cigarettes were smoked to a butt length of 23 mm (CORESTA standard method).

Analytical Methods

The cigarette smoke condensate (CSC) was fractionated by the method of Snook (12). The WAc fractions were analysed by GC-chromatography on a Varian 3400 model instrument with:

- capillary column DB1
- Column conditions: initial temperature 250°C (isothermal for 3 min), 15°C/min to 300°C
- carrier gas - hydrogen, 3 ml/min

The mass spectra were obtained on a mass spectrometer Mod. Finigan MAT 8230, under the same conditions as the GC-analysis.

Thermal decomposition of tobacco was performed on Perkin-Elmer thermograph Mod. TGS-2 with air flow as in single puff.

Statistical analyses of multiple correlation were done on personal computer PC-12.

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levels of these two elements in tobacco leaves and not least also in cigarette smoke and its condensate is very important for studies connected with pulmonary absorption and the health effects of volatile elements (toxic or essential) on living organisms. It is also relevant to aspects of the uptake of trace elements by plants.

In collaboration with the Tobacco Factory from Rovinj some types of Burley tobacco cultivated in the Istrian peninsula were analysed for As and Sb, and the results obtained were compared with the values for Burley and other sorts of tobaccos from different geographical regions (Table 1).

From the data for As and Sb in common Burley, Prilep and Virginia tobaccos from different regions it is evident that the concentration levels for these elements are practically the same. In comparison with our previous results (7) the concentration levels for As and Sb decrease because of the decreasing use of As-containing herbicides in the protection of tobacco plants. In cultivated Istrian Burley treated with As and Se, the results for As obtained show differences in concentration levels between lower, middle, and upper leaves and their veins which depend on the sort of tobacco and strongly on the soil texture and its iron and phosphorus content. The preliminary results for these two elements in filter butts and tar after smoking show rather low values and this suggests that the transfer of these two elements into smoke condensate and further into human body is small, though their amounts in smoke need investigation.

Analyses of shredded noncertified reference Kentucky Tobacco 2R-I and two candidate tobacco materials (CTA-OTL-1, CTA-VTL-2), prepared by the Polish Academy of Science were also performed.

The accuracy of results obtained was checked by the analysis of different SRMs and good agreement with certified values was obtained; this proved the reliability of the radiochemical separation procedure for determination of As and Sb in biological materials developed previously in our department.

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LITERATURE

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SORBITOL EFFECTS ON TAR, NICOTINE AND CARBON MONOXIDE YIELDS OF CIGARETTES

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SUMMARY

The aim of this investigation was to establish whether sorbitol effects changes in tar, nicotine and carbon monoxide yields of cigarettes.

The testing was carried out in the laboratory, on experimental filter cigarettes, made up of Croatian tobaccos of different grades and different leaf groupings. The experimental blend consisted of 70% Virginia and 30% Burley. Sorbitol, a 70% water solution , was applied by spraying. Tobacco mixture was treated with 1%, 3% and 5% sorbitol, respectively.

The results obtained indicate that aforesaid concentrations of sorbitol in the tobacco mixture do not effect any significant changes in tar, nicotine and carbon monoxide yields of a cigarette.

INTRODUCTION

An optimum moisture content of tobacco is an essential prerequisite for efficient handling, manufacture and storage. Insufficiently moist tobacco is brittle and its taste is unacceptable. Too great a moisture content of tobacco has a negative effect on combustibility, causes colour changes in tobacco, and leads to microbiological changes.

Maintaining an optimum tobacco moisture content is an unavoidable problem in cigarette manufacture. Cigarette manufacturers solve it by adding humectants. The function of humectants is to improve the tobacco's hygroscopic properties. Tobacco, just like other natural materials, is very sensitive to changes in the moisture content of the air surrounding it. Humectants are therefore added to decrease the influence of atmospheric conditions on tobacco. The humectants most frequently used in cigarette manufacture are various alcohols: glycols, glycerol and sorbitol.

Sorbitol belongs to the group of sugar alcohols. It is widespread in nature and is a constituent part of numerous plants, including tobacco. It is chemically stable, thermostable and practically non-volatile, so it is quantitatively retained in tobacco even during processes taking place at increased temperatures. Sorbitol combustion products are akin to the combustion products of the sugars present in tobacco. The above mentioned properties make sorbitol an acceptable additive to tobacco.

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the portion of the neutral fraction (X_1 mg/cig) and the nicotine content in the neutral fraction (X_2 mg/cig) we arrive at the following equation :

Equ. 1 :

$$X = 11,6477 - 0,0758\ X_1 + 0,6444\ X_2$$

$$R_{1,2,3} = 0,9946$$

$$r_{1,2} = -0,9843$$

$$r_{1,3} = 0,7979$$

$$r_{2,3} = 0,6991$$

The conclusion is that the dependence of "completeness" on both factors is well defined with a very marked negative correlation with the portion of the neutral fraction in CSC and pronounced influence of nicotine in it. The dependence among the two factors themselves is medium ($R_{2,3} = 0,6991$).

For strength (y) the equation is :

Equ. 2 :

$$Y = -1,8115 + 0,0647\ X_1 + 0,0166\ X_2$$

$$R_{1,2,3} = 0,8546 \qquad r_{1,3} = 0,7079$$

$$r_{1,2} = 0,8365 \qquad r_{2,3} = 0,8679$$

The dependence between the portion of neutral fraction and nicotine content in it is, in this case, more important ($r_{2,3} = 0,8679$), which can, again, be explained by the camouflage effects of the other components found in the neutral fraction.

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RESULTS AND DISCUSSION

Air samples were collected from several smoking and nonsmoking environments, including restaurants, bars, cars, offices, homes, laboratories, and an indoor garage. Table 1 shows the levels of benzene, alkylbenzenes, pyridine, picolines, 3-vinylpyridine, limonene, and nicotine.

Among several different adsorbents (Carbopack 8, Carboxen 564, carbosieve III, molecular sieve 5A), Tenax TA was found to be the most effective one; however, it is not suitable for trapping smaller molecules such as 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, furan, isoprene, acrylonitrile and acetonitrile. Aging studies showed that ETS samples collected on Tenax TA were stable for a week when kept refrigerated. As can be seen in Table 1, benzene and some alkylbenzenes are ubiquitous, ranging from 3 to 167 $\mu g/m^3$; the levels of pyridine and picolines observed in ETS are significantly lower in comparison (up to 16 $\mu g/m^3$). It should be pointed out that benzenes and pyridines are by no means specific to tobacco smoke since they are produced by other sources, such as automobile exhaust.

Limonene was detected at considerable levels in a restaurant (both in smoking and nonsmoking sections) and a new car which we attribute to the use of lemon-scented cleaning agents, although limonene is also present in cigarette smoke. Except for a laboratory, limonene was found present in all other samples, ranging from 2-94 $\mu g/m^3$. The laboratory air sample had the lowest overall levels of the compounds analyzed in this study, most likely because of the frequent air exchanges.

Nicotine in smoking environments was present from 14-117 $\mu g/m^3$. This compares well with other studies; Thompson *et al.* found up to 37 μg nicotine/m^3 in restaurants (11) while Eatough measured nicotine in discos and found up to 119 $\mu g/m^3$ (7). In a nonsmoking area of a restaurant we found up to 6 μg nicotine/m^3, possibly due to contamination effects from the adjacent smoking section. In an office officially labeled nonsmoking, we detected 3.7 μg of nicotine/m^3; we assume that this is due to some limited smoking activity.

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INFLUENCE OF RECONSTITUTED TOBACCOS ON CIGARETTE BLEND

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SUMMARY

The objective of this work was to study several experimental blends containing different types of reconstituted tobaccos. The reconstituted tobaccos arose from two slurry proccesses and a paper-like proccess of manufacturing. A special sauce, that simulates a casing recipe, was added to two of the reconstituted tobaccos before blending. Also an inorganic salt, solved in the former casing, was used as a tracer of the reconstituted materials in the final blend.

Six batches of tobacco blends were used in this study. The first was a blend of natural bright tobaccos, and the other five were a blend 1:1 of the above described materials. Sizes distributions of the blends are obtained by sieving. An HPLC method, using conductimetric detection, provided the concentrations of several inorganic anions in the different size fractions of the blends. Propylglycol anc bencylalcohol were also measured, via a GC method, in the same fractions of tobacco shreds.

The whole set of data gives some insight in the blend composition. Also the mechanical degradation of the reconstituted tobaccos is shown by compairing the distributions of the measured variables. In addition, the results for some of the components of the casing, measured in the total blends, provide some meaningful information about the ability of the reconstituted tobaccos in adsorbing certain types of casings.

INTRODUCTION

Reconstituted tobacco has been used increasingly for economical reasons in the manufacture of cigarettes, and as a result has been called the cigarette filler of the future (1). The proportion in which it is used in a blend (1,2,3) depends on the characteristics of the product used and its effects on organoleptic characteristics.

The study presented here concerns the effects of using various types of reconstituted tobaccos on the chemical composition of a blend, and their effects on stiffness of a blend of bright tobacco. Also studied here is the relationship between distributions found for the composition of various anions (5) and other compounds normally added to sauces (7), and the characteristics of each type of reconstituted tobacco used. A geometric model of shreds is proposed allowing for the interpretation of the distribution of humectants found in terms of surface adsorption, which explains the variations observed in the distribution of shred size within the total blend of cigarette filler depending on the type of reconstituted tobacco used and the dosage of sauce used.

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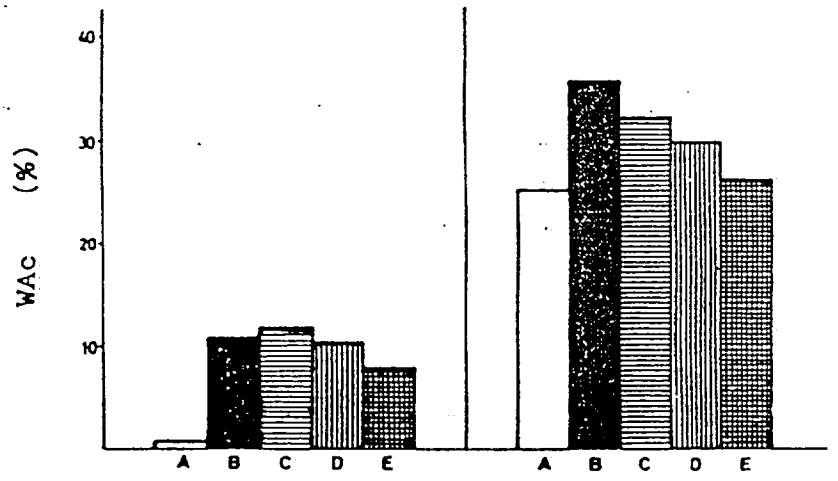
It is appropriate to first examine the big increase in number of the components of the WAc fraction. This fraction of untreated tobacco is both low in number and concentration of components. We found 65 compounds of which only 20 were found at an important concentration. The WAc fraction of tobacco treated with glucose, fructose, sacharose, and sugar syrup contains 98 compounds. Among these components cyclic diketones and phenols have a significant portion. From the Figure 3 it is seen that the addition of sugars causes increase of 10,95 % in cyclic diketones and increase of 10,53 % in phenoles.



Diketones Phenoles

A-o,87 ..... 25,o6
B-10,98 35,59
C-11,82 32,14
D-10,22 29,64
E-7,93 26,01

The fact that in pure tobacco only 2-cyclopentene-1-on-3,4, 5-trimethyl was identified in low concentration of 0,87 % (MS - Fig. 4) and that in all treated tobaccos samples the 2-cyclo pentene-1-one-2 hydroxy-3 methyl (MS - Fig. 5) was identified (x) [both in concentrations up to 7,02 %], points out the presence of the mentioned mechanism in Fig. 1.

(x) in addition to above mentioned

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INFLUENCE OF NICOTINE CONTENT IN THE NEUTRAL FRACTION OF CSC ON COMPLETENESS AND STRENGTH OF SMOKE TASTE

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SUMMARY

Organoleptic properties (primarily "completeness" and strength) of a large number of cigarettes of various smoke qualities have been examined. The nicotine content in the neutral fraction of cigarette smoke condensate (CSC) from these cigarettes was determined by GC. Separation of the neutral fraction was done under the approximate conditions that occur in the oral cavity (temperature, pH, presence of enzymes, ...). Investigation showed a high correlation between the nicotine content of the neutral fraction and smoke irritation and "completeness" and a medium correlation with smoke strength. The level of correlation differed amongst the different quality groups.

INTRODUCTION

Undoubtedly tobacco alkaloids are most often tested and investigated in tobacco and tobacco smoke (4, 5, 6, 8). These investigations encompassed organoleptic properties, too. However, the results are obscure, probably due to the complexity of the problem itself (difficulty in distinguishing alkaloid

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TABLE 1 : Sidestream smoke yields per cigarette as obtained using the single cigarette total collector device (TCD), the experimental chamber (E.Ch.) and ETS experiments (ETS) (*)

Cigarettes	Conditions	CO (mg)	APM (mg)	NOx (ug)	NIC. (ug)	NH3 (ug)	HCN (ug)
C20	TCD	60	33.2	1760	4800	6400	n.a.
	E.Ch.	63	14.2	1850	3400	5800	270
	ETS	58	9.2	1560	390	4930	260
C50	TCD	53	30.4	1720	4500	n.a.	n.a.
	E.Ch.	53	13.7	1740	3500	6000	240
	ETS	47	8.9	1350	280	n.a.	n.a.

n.a. : not analysed (*) : Average of all experiments with room ventilation < 6 ACH

Using 24 mg as SS APM yield (value being derived from several surveys of commercial products), Repace has proposed an empirical formula to estimate the equilibrium RSP concentration in steady state situations (11):

$$C_{equ}\ (ug/m^3) = 650\ D/c_v \qquad \ldots [5]$$

D being the number of burning cigarettes per 100 m^3 of space. In our case, the C20 cigarettes used in the steady state experiments have a higher than normal APM yield of 33.2 mg so that the proposed model would be valid if:

$$C_{equ}\ (ug/m^3) = 900\ D/c_v \qquad \ldots [6]$$

Table 2 shows that equation [6] yields equilibrium concentrations that are 110 to 160 % too high, indicating that this empirical formula is grossly overestimating exposures mainly due to its failure to take into account the intrinsic difference between SS and ETS as discussed above.

TABLE 2 : Equilibrium concentrations for ETS RSP (ug/m3)

Generation rate	Comp. using [6]	Exp. data	Difference (%)
4 cig/hour	616	293	110
3 cig/hour	447	208	115
6 cig/hour	955	366	161

Nicotine

The nicotine results can be interpreted in the same way as the RSP data. Table 1 shows that even after attempting to correct for early decays, only 74% of the nicotine yield can be accounted for in the experimental chamber. It is clear that in this case the exponential extrapolation is flawed: the kinetics for wall adsorption change very fast in the early phase of the decay. For ETS, this results in even lower apparent emissions: On average for all results, the model only calls for 7.5% of the cigarette delivery.

Nitrogen oxides

In order to compare the different sets of data, the concentration of all nitrogen oxides (NOx) pooled together was taken into account. Although NOx are reactive compounds, their decay is well approximated by the exponential model in the chamber. Table 1 yet shows ETS results are still 10-20 % low.

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LES RÉSULTATS DE L'ÉVALUATION D'EXPERTS EN DÉGUSTATION MONTRENT UNE DIFFÉRENCE DANS LES PROPRIÉTÉS DE FUMAGE ENTRE LE TÉMOIN ET LA CIGARETTE EXPÉRIMENTALE. CES DIFFÉRENCES NE SONT PAS DANS LE MÊME SENS POUR TOUS LES EXPERTS PAR RAPPORT À LA MÊME MANIFESTATION DES SENSATIONS. LE DEGRÉ MOYEN DE LA DIFFÉRENCE CONSTATÉE (EXPRIMÉ EN POINTS POUR LES TROIS DEGRÉS DE CHAQUE PROPRIÉTÉ - ARÔME, GOUT, INTENSITÉ) NE DÉPASSE PAS 2 POINTS, CE QUI MONTRE QUE LES DIFFÉRENCES SONT MINIMES OU BIEN UN PEU PLUS PRONONCÉES, MAIS NE SONT PAS DISTINCTEMENT MANIFESTÉES.LE SENS DES DIFFÉRENCES, C.-À-D. MIEUX OU PIRE PAR RAPPORT AU TÉMOIN EST PLUS SOUVENT AU PROFIT DU TRAITEMENT. LA CIGARETTE À MÉLANGE EXPÉRIMENTAL EST SANS DOUTE MEILLEURE.

LE CRITÈRE STATISTIQUE (COEFFICIENT DE STUDENT) EST INFÉRIEUR À 1,96 INDÉPENDAMMENT DE LA PRÉFÉRENCE PRÉDOMINANTE POUR LE TÉMOIN OU POUR LA CIGARETTE ESSAI. CELA MONTRE QUE LES DIFFÉRENCES ENTRE LES CIGARETTES ESSAI (TRAITEMENTS) PAR RAPPORT AUX PROPRIÉTÉS DE FUMAGE SONT IMPERCEPTIBLES.

CONCLUSIONS

LES RÉSULTATS OBTENUS CONCERNANT L'EFFET DES FACTEURS ÉTUDIÉS SUR LA COMPOSITION DE LA FUMÉE SONT À LA BASE DES CONCLUSIONS SUIVANTES:

1. LA RÉDUCTION LA PLUS IMPORTANTE DES GOUDRONS (22,58%), DE LA NICOTINE (9,10%) ET DU MONOXIDE DE CARBON (14,46%) EST ATTEINTE SUITE À LA MODIFICATION DE LA COMPOSITION DU MÉLANGE, L'UTILISATION DE CÔTES EXPANSÉES ET D'UN ADDITIF AU TABAC AVEC LE FILTRE 3/32.000 D.P.F.

2. LE RÔLE LE PLUS IMPORTANT DANS LA RÉDUCTION EST CELUI DE LA MODIFICATION DU MÉLANGE (50% ENVIRON DE LA RÉDUCTION TOTALE), SUIVI PAR CELUI DE L'ADDITIF (40% ENVIRON). L'EFFET DES AUTRES FACTEURS N'EST PAS SI BIEN MANIFESTÉ.

3. L'UTILISATION DE 10% DE CÔTES EXPANSÉES À 20% NE RÉDUIT PRATIQUEMENT PAS LES SUBSTANCES DANS LA FUMÉE.

4. IL N'Y A PAS DE DIFFÉRENCE SIGNIFICATIVE ENTRE L'EFFICACITÉ DE RÉTENTION DU FILTRE À 3/35.000 D.P.F. ET CELUI À 3/32.000 D.P.F., MAIS TOUS LES DEUX SONT PLUS EFFICACES QUE LE FILTRE

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PHENOLS IN TOBACCO SMOKE - POSSIBLE ROUTE FOR THEIR SYNTHESIS FROM ADDED SUGARS

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SUMMARY

The phenol content of cigarette smoke condensate (CSC) from cigarettes made of Burley tobacco treated with four types of sugar casings has been determined by GC. As the increase was up to 10 % and the pH of the samples between 5,20 - 5,50 we supposed that base-catalyzed sugar degradation can be an explanation for phenols arising by pyrolysis. By identification of components of the weak acid (WAc) fraction of CSC (MS - identification), particulary by identification of 3-methyl 4,4-dimethyl-2-cyclohexene-1-one and 2-cyclopentene-1-one-2-hydroxy-3-methyl, and some other cyclic diketones, we consider this possibility confirmed.

INTRODUCTION

A survey of literature indicates that 5-methylfurfural and 5-hydroxymethylfurfural are the major products of sugar pyrolysis (4, 6, 13). Chemical changes under conditions of weakly acidic media are either dehydratation of monosaccharides or reactions with amino compounds (Maillard reaction - 2, 9). In more acidic or alkaline media the process of caramelization can be directed more towards aroma formation or more towards browning pigment accumulation. Increasing interest for treating lower grades of Burley tobacco, especially in Yugoslavia, with casings extended our efforts to identify some other mechanisms of sugar pyrolysis. In such cases the lower absorbing power of tobacco cell tissue retains sugars more at the leaf surface; the pH is near to neutral or slightly alkaline and additives increase a high-temperature thermolysis (5). We will report the results of our investigation of the WAc fraction of CSC of Burley tobacco treated with sugars under supposedly base-catalyzed degradation.

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À 3,9/35.000 D.P.F.

5. L'INFLUENCE DE L'ADDITIF (1% PAR RAPPORT À LA MASSE DU TABAC) EST NETTEMNT POSITIVE ÉTANT CAUSE D'UNE RÉDUCTION DE 11,01% DES GOUDRONS ET D'UNE RÉDUCTION DE 6,62% DE LA NICOTINE.

6. LES MODIFICATIONS DU MÉLANGE, L'UTILISATION DE CÔTES EXPANSÉES, D'ADDITIF ET DE FILTRES N'ENTRAÎNENT PAS DES MODIFICATION DES PROPRIÉTÉS CARACTÉRISTIQUES AU TYPE ET À LA MARQUE ET PEUVENT, PAR CONSÉQUANT, ÊTRE UTILISÉS AVEC SUCCÈS.

TABLEAU 1
COMPOSITION DE LA FUMEE DE CIGARETTES
DES DIFFERENTS TRAITEMENTS

TRAITEMENTS*	COMPOSITION DE LA FUMÉE, MG/CIG.			
	CONDENSAT SEC	GOUDRONS	NICOTINE	CO
No.1357(TÉMOIN I)	32,43	31,00	1,43	21,99
No.2357(TÉMOIN II)	29,28	27,91	1,37	20,72
No.2358	28,41	27,04	1,37	20,64
No.2368	25,99	24,68	1,31	20,01
No.2458	28,21	26,85	1,36	21,00
No.2459	28,53	27,22	1,31	19,83
No.2468	26,48	25,21	1,27	15,20
No.2469	25,34	24,06	1,28	18,81

*LES TRAITEMENTS SONT MARQUÉS PAR UN CODE DONT LES CHIFFRES REPRÉSENTENT LES ÉLÉMENTS RESPECTIFS (FACTEURS) DE LA COMBINAISON DE LA FACONDONT ILS ÉTAIENT PRÉSENTÉS CI-DESSUS.

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the room, where potential receivers would be. It happens here in spite of a very efficient mixing (2 fans blowing) and while the measuring spot was only 1.5 m from the source. More complex models can take this effect into account but they are not amenable to real situations (16).

Aerosol particulate matter

APM or its respirable part RSP (APM with an aerodynamic diameter < 3.5 u) have been the main target of model studies on ETS.

For APM removal, k is larger than c_v. This difference which one needs to estimate for any modelling varies with experimental conditions. It reflects losses to surfaces and evaporation (17). In air tight chambers (c_v = 0) values of 0.1 to 0.2 ACH have been reported for k (1,2) in agreement with our chamber data (0.1 ACH (4)). In this case evaporation is very limited.

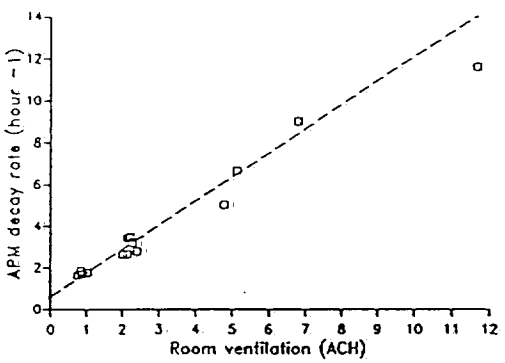

FIGURE 2: APM decay rate vs. room ventilation

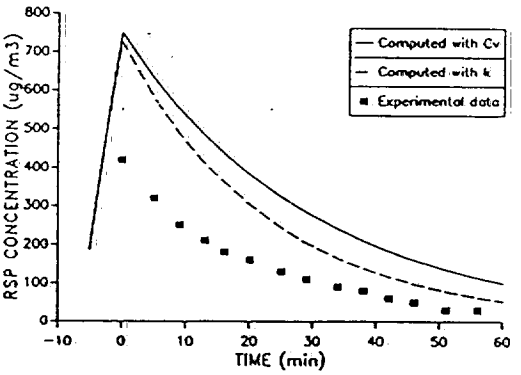

FIGURE 3: Actual and predicted APM decay

Figure 2 shows the k values computed from APM decay plotted as a function of c_v. In agreement with (10), these results show a linear relationship with a 0.6 ACH intercept. The difference between k and c_v averages 0.8 ACH with no clear influence of c_v on this value. Some models (11) assume that the ratio of k to c_v is constant. This is not supported by our data set. APM yields computed from the experimental chamber results are only 45% of the fresh SS yields, in agreement with (5, 17,18). This effect is further pronounced in ETS situations: figure 3 shows experimental data from a pulse experiment compared to the concentrations computed using either c_v (room ventilation) or k (from APM decay) as decay rates. The emission used for the calculation is that derived from chamber results. On average for all pulse experiments with less than 6 ACH, only 65% of the emission computed from the experimental room results, i.e. 30% of the actual SS yield, are actually found as ETS RSP. At very high ACH, the ratio drops further, due to clearance before mixing as discussed above. These results are summarised in table 1, as well as the computed yields of all other components studied.

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TABLE 2
CHROMATOGRAPHIC PARAMETERS

PEAK NUMBERS	SUGARS	T_r[a] (min)	k'[b]	t_R[c]
1	Inositol	1.707	0.104	0.188
2	Xylitol	1.888	0.221	0.205
3	Sorbitol	2.230	0.442	0.259
4	Mannitol	2.450	0.585	0.295
5	Trehalose	2.621	0.695	0.330
6	Fucose	2.621	0.695	0.580
7	2-Deoxy-D-Ribose	2.887	0.867	0.688
8	2-Deoxy-D-Galactose	3.040	0.966	0.768
9	Rhamnose	3.204	1.072	1.000
10	2-Deoxy-D-Glucose	3.559	1.302	1.125
11	Arabinose	3.559	1.302	1.152
12	Galactose	3.984	1.577	1.286
13	Lyxose	4.225	1.733	1.393
14	Glucose	4.225	1.733	1.438
15	Xylose	4.298	1.780	1.509
16	Fructose	4.625	1.992	1.554
17	Allose	4.987	2.226	1.643
18	Ribose	5.165	2.341	1.744
19	Melibiose	5.406	2.497	1.744
20	Sucrose	6.766	3.376	1.955
21	Lactose	7.206	3.661	2.321
22	Cellobiose	9.670	5.255	2.723
23	Gentiobiose	10.181	5.585	2.795
24	Raffinose	11.604	6.506	2.893
25	Maltose	15.992	9.344	3.554

[a]T_r=retention times in isocratic elution; [b]$k' = (t_- - t_-)/t_-$, where t_-=retention times of carbohydrates and t_-=retention time of eluent in isocratic elution; [c]t_R=retention times relative to rhamnose in gradient elution

RESULTS AND DISCUSSION

Several samples, obtained from different cultivars, were assayed. Typical chromatograms of some main cultivars are shown in figures 3-7. Some mono and disaccharides were identified from their retention times; the main were inositol, glucose, fructose, sucrose and galactose, the latter only in samples of Burley. Some quantitative determinations of glucose, fructose, inositol and sucrose were carried out for cultivars of Oriental tobaccos, Bright and Kentucky. The range of concentrations are given in table 3.

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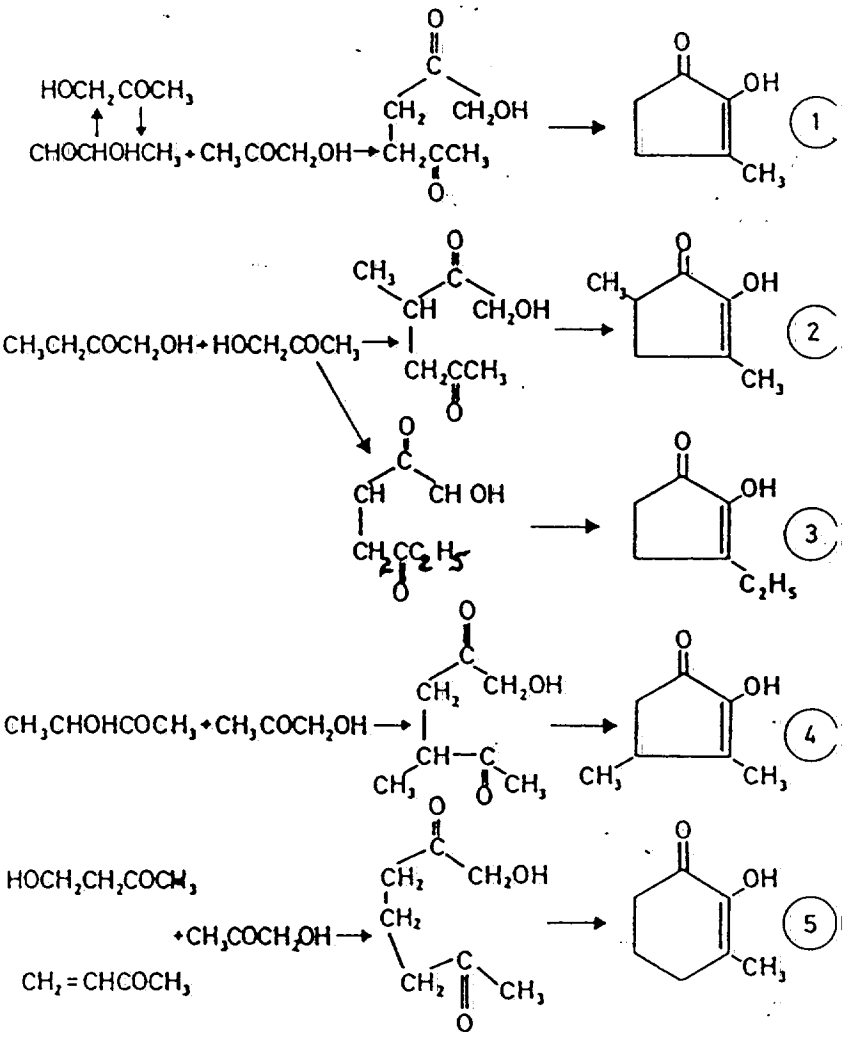
BASE-CATALYZED SUGAR DEGRADATION

A suitable model system for base-catalyzed fructose degradation was reported by Philip Shaw and coworkers (10). Under initial weakly alkaline conditions, with no extra addition of bases, the major porducts of degradation were as shown in Figure 1.



Under nonoxidative conditions in slightly alkaline media at elevated temperatures hydroxyaldehydes and hydroxyketones arise from cleavage of the carbon chain of sugars. Since enolization is not restricted to any part of the molecule and, since water elimination is not restricted in amount, even the spectrum of primary cleavage products is remarkable. By aldol condensation and intramolecular Cannizaro reactions (Fig. 1)

Figure 1: Base-catalyzed sugar degradation

these highly reactive products provide a great number of other products, for example cyclopentenolones (1).

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INFLUENCE OF BAROMETRIC PRESSURE ON THE DETERMINATION OF CIGARETTE SIDESTREAM-SMOKE

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SUMMARY

An experiment was carried out in order to quantify the influence of barometric pressure on the determination of cigarette sidestream-smoke. Two different locations at 650 m and 10 m above sea level, respectively, and three different cigarettes, including commercial brands and the 1R4F reference cigarette, were selected for the experiment. A modified "fishtail" chimney device was used for the collection of sidestream smoke.

Results of mainstream deliveries confirmed previous research on the topic, showing significant differences in puff-count. Significant differences were also detected in some sidestream yields as a consequence of the influence of barometric pressure.

Two different chimney flow rates were investigated at the higher altitude laboratory in order to obtain the same sidestream yields as those obtained at the lower one. An increase in the flow rate was found to be a way to neutralize the influence of low barometric pressure.

INTRODUCTION

Barometric pressure is one of the conditions specified by ISO 4387 and ISO 3402 regarding the atmosphere of a smoking enclosure. The accepted range, according to ISO 3402, for barometric pressure in test atmospheres is from 860 to 1060 mbar, i.e. 645 to 795 torr. The lower limit of this range normally corresponds to an altitude of 1300 m above sea level.

Barometric pressure has a noticeable effect on the analytical smoking of cigarettes. As was established in a previous study, the lower the barometric pressure the higher the puff-count and the higher the debilitation of mainstream puffs (1).

The aim of this study was to examine the effect of barometric pressure - within the above mentioned accepted range - on the determination of cigarette sidestream-smoke.

EXPERIMENTAL SET UP

A test was planned in order to study the reproducibility of cigarette sidestream-smoke determination at two locations: Madrid and Sevilla at +650 m and +10 m above sea level, respectively, covering a range of barometric pressure from 690 to 755 torr. Obviously, Tabacalera´s smoking analysis laboratory in Madrid was selected as a reference point, and another smoking laboratory was provisionally installed in the Quality Control laboratory of the Sevilla´s cigarette factory as an alternative location.

Theree samples were selected including two commercial cigarettes: AB, an American-blend full-flavour cigarette; DAC, a dark air-cured cigarette; and the 1R4F reference cigarette. A summary of their typical mainstream yields

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A 15-cm pathlength, single-path, transmission gas cell is located in the sample compartment of the spectrometer. The gas cell is equipped with screw-on end caps that contain the KCl windows. A reference spectrum of the gas cell with new windows is stored for comparison with a spectrum of the gas cell after prolonged use to determine when the windows need to be replaced. The gas lines to the sample cell are connected at the sample compartment wall by push-button operated quick-disconnect fittings.

RESULTS AND DISCUSSION

There are two main considerations in the use of a FT-IR spectrometer for quantitative analysis (1). The first is that the instrument must have an adequate signal to noise (S/N) ratio to allow for an accurate determination of absorption line peak areas at the minimum concentrations to be analyzed. Second, the resolution must be adequate to resolve individual analyte absorption lines from those of other infrared absorbing gases present in smoke. The two performance parameters are related in that an increase in resolution decreases the S/N ratio. The S/N ratio of an FT-IR spectrometer decreases with the square root of the number of individual scans that are coadded. For this application, the number of scans that can be collected is limited by the 60 second smoking cycle of the smoking machine.

The signal, i.e., the absorption line peak height of the analyte, is controlled by the amount of sample delivered and the pathlength of sample cell. Most low-molecular weight gases exhibit a series of narrow absorption lines as shown in Figure 2 for hydrogen cyanide. For quantitative analysis of most gas samples, the analyte concentrations must be low so that the peak areas are linearly, or approximately, linearly related to concentration. The effect of absorption levels on the linearity of peak area versus concentration is shown in Figure 3. Low-cost FT-IR spectrometers are generally limited to 2 cm^{-1} resolution. Absorption peaks that are narrower than 2 cm^{-1} appear to have a peak width of 2 cm^{-1} when collected at 2 cm^{-1} resolution (Figure 2). The net area of the peak remains the same but there is significant loss in peak height. It is for this reason that peak areas, rather than peak heights, are used for determining the concentration of the gas samples. Sample data were collected at 2 cm^{-1} resolution. This is adequate to resolve each of the analyte gases from interfering peaks. Less resolution is not adequate to resolve the NO absorption peaks from the surrounding water vapor absorption peaks.

Calibration data were obtained by mixing reference gases with nitrogen using a mass flow control system. Plots of peak area versus concentration are shown in Figure 4. Wavelengths used for each gas and the calibration equations are given in the legend of Figure 4. The corresponding regions of the smoke spectrum along with the reference gas spectra are shown in Figure 5. Acetaldehyde has a broad absorption line and is linear over a wide range in concentrations. The levels of NO are sufficiently low that a linear relationship is found over the range of concentrations encountered in cigarette smoke. A simple linear fit of the calibration data is used to determine the levels of these two cases in cigarette smoke. The relationship

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obtained in Madrid and their physical and dimensional characteristics can be observed in the Table 1 below.

TABLE 1 : Cigarette characteristics

		Samples		
		AB	DAC	1R4F
Total weight	[mg]	1030	990	1090
Pressure drop	[daPa]	110	115	135
Total length	[mm]	84	79	84
Filter length	[mm]	21	20	27
Tipping length	[mm]	25	24	32
Butt length	[mm]	29	28	35
Puff count	[mm]	9.3	7.7	9.2
Smoke nicotine	[mg/cig]	1.2	0.6	0.9
PMWNF	[mg/cig]	17	11	10
Carbon monoxide	[mg/cig]	15	15	12

All the samples and 44 mm Cambridge filters were conditioned at 22° C and 60 % relative humidity in Madrid. Then the cigarettes were hermetically sealed in groups of one hundred.

A schematic layout of the experimental set up is shown in Figure 1.

A portable four-ports Borgwaldt RM 4 CS smoking machine was selected in order to enable quick and easy installation. The small number of ports meant the performance of many smoking runs, but this smoking machine was preferred owing to its portability.

The well known "fish-tail" chimney device (2) was used for the collection of sidestream smoke. For this particular experiment a big chimney 120 mm wide at the lower opening and 500 mm long was modified in such way that a hinged plate could be positioned at a distance of 6 mm from the lower opening in order to avoid sidestream leakages. This also ensured that the cigarettes were smoked in a fresh air surrounding.

A Hewlett Packard gas-chromatograph with flame ionization, thermal conductivity and thermoionic detectors was used for the analyses of nicotine and water.

A Leyboldt Binos carbon monoxide-carbon dioxide analyzer, including a thermostabilized pump, was used for gas phase analysis - both, mainstream and sidestream -, and a Gillian Aircon high pressure-drop pump connected to a latex-made 250 litre bag was used for the collection of sidestream smoke. A Hewlett-Packard computer processed gas-phase data for noise and integration treatment on line.

Some auxiliary measuring apparatus such as an analytical balance (Mettler), a thermohygrometer (Lambretch), a barometer (Lambretch), an anemometer (Airflow) and a electronic bubble flow meter (Gillian) were used in both locations.

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The carbon content of the burning cone was almost constant. However, the carbon content of the ash increased slightly with an increasing amount of alkali metal (Table 2).

FIG. 4
DSC CURVES OF SAMPLE B
(CHAR MADE FROM TOBACCO TREATED WITH POTASSIUM MALATE)

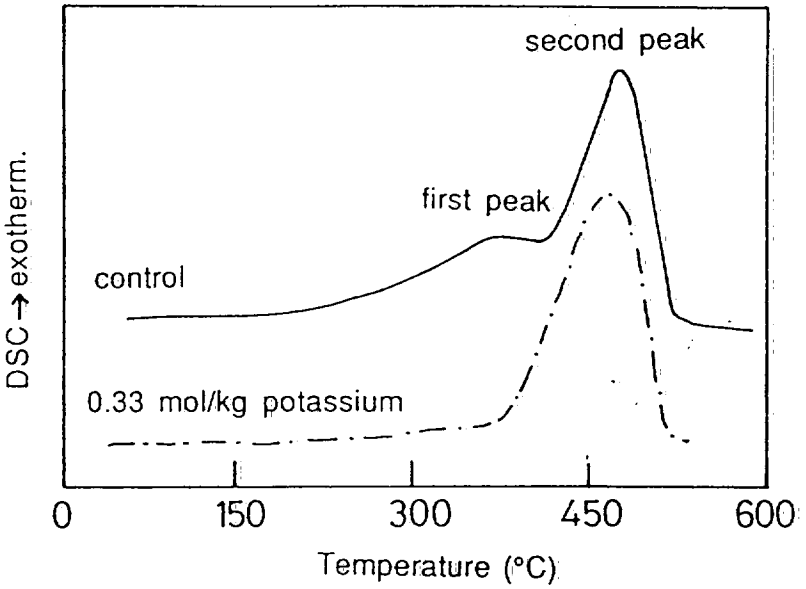
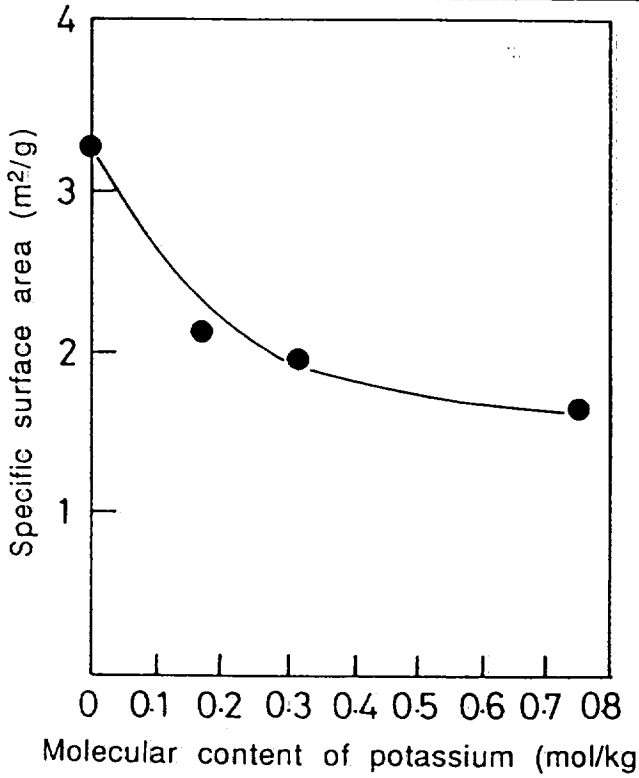


FIG.5
SPECIFIC SURFACE AREA OF TOBACCO CHAR



Yields of char from the extinguished burning cone were estimated from the alkali metal content of the burning cone. The yield of char in the burning cone was about 28% and was independent of the amount of additive alkali metals.

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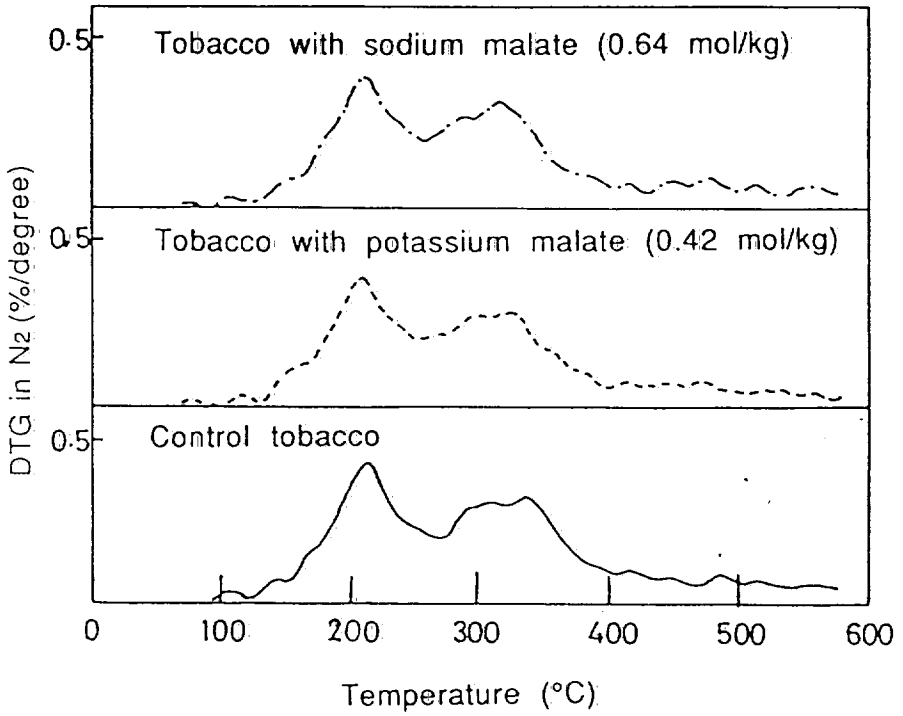
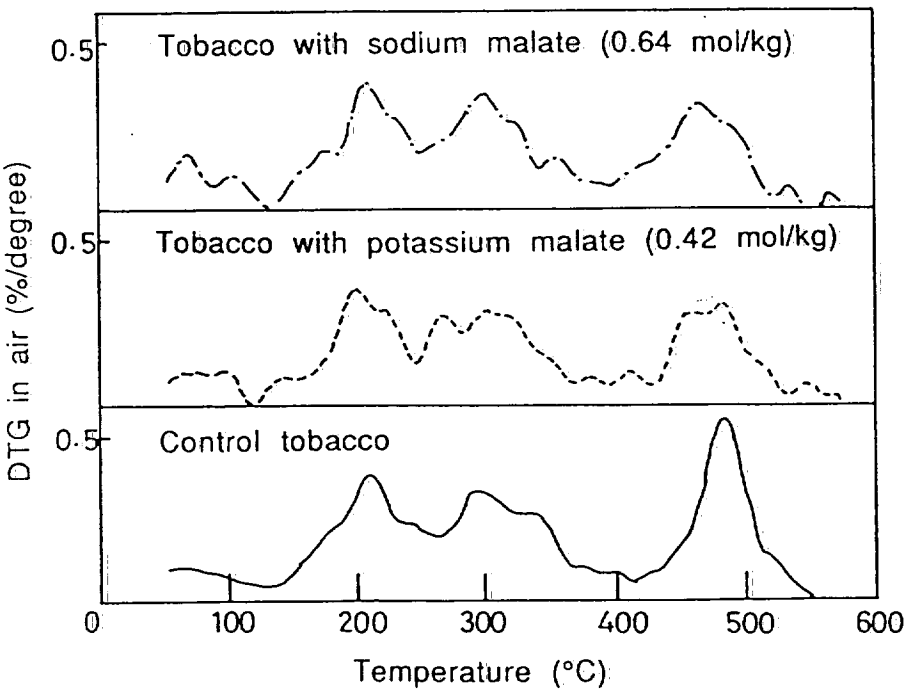
FIG. 2

DTG CURVES OF TOBACCO WITH AND WITHOUT ALKALI METAL SALT ADDITIVES





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ANALYSIS OF LOW MOLECULAR WEIGHT CARBOHYDRATES OF TOBACCO BY HIGH PERFORMANCE ION CHROMATOGRAPHY

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Monopoli di Stato - Divisione Ricerche - Roma - Italy

SUMMARY

The aim of the present work is to develop a High Performance Ion Chromatography method for the qualitative and quantitative determination of both reducing and non-reducing low molecular weight carbohydrates in tobacco leaf.
Detection and identification of these compounds was carried out using a DIONEX 4000 Ion Chromatograph equipped with a pulsed amperometric detector. Columns used were HPIC-AS6A (150x4mm, 5µm particle size bed) or HPIC-AS6 (250x4mm, 10µm particle size bed) with guard columns HPIC-AG6A and HPIC-AG6, respectively. Both columns used amino modified polystyrene-divinylbenzene phases.
The amperometric detector uses a multistep potential wave form of three different voltages, each applied for a few milliseconds, resulting in alternating anodic and cathodic polarizations. This allows the amperometric detection of the $-CH_2OH$ functions of carbohydrates and the cleaning and reactivation of the electrode surface.
Sodium hydroxide solutions were used to improve the anion separation of carbohydrates which behave as weak acids with a pKa in the range 12-14.
Both isocratic and gradient elutions were run using different effluent flows in the range 0.5-1.0 ml/min. The sensitivity of the detector was also increased by adding a more concentrated solution of sodium hydroxide at the end of the separator column. This resulted also in a reduction of baseline drift.
Twenty-two carbohydrates were separated by isocratic elution and twenty-four by gradient elution.
Some chromatograms of standard compounds are shown, together with samples obtained from cultivars of Bright, Kentucky, Maryland, Paraguay, Burley, and Oriental tobaccos. Some mono- and disaccharides were also identified from their retention times. Some quantitative determinations for glucose, fructose, inositol, and saccharose were carried out for the above cultivars. Results were in the range 2-17%, 1-13%, 0.5-2%, 0.5-6%, respectively.

INTRODUCTION

Carbohydrates make up a large proportion of the leaf of many tobacco varieties, both as free or in the combined state, and are of great interest because of their relationship to leaf quality

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Les résultats de ces expériences sont comparés et les implications concernant l'estimation des expositions sont discutées.

INTRODUCTION

The investigation of the build-up and decay of environmental tobacco smoke (ETS) components has been the subject of numerous studies, both in rooms and in experimental chambers (1-9). Some mathematical models were proposed in order to describe these effects (10-12), and predictions of ETS levels were even made from minimal sets of parameters (number of air changes per hour (ACH) and room volume, number of cigarettes smoked per hour) (11). The objective of this study is to provide a comprehensive data base on the SS deliveries of experimental cigarettes, as measured under various environmental conditions. It is then to identify some pitfalls that may be encountered when trying to predict ETS exposures.

EXPERIMENTAL PROCEDURES

Experimental cigarettes

The 2 experimental cigarettes used for this study were made from virtually the same american-type blend, with no flavour or humectant addition, and designed to have filter dilutions of 16 (C20) or 46 % (C50). Kept frozen at -40 °C, they were equilibrated at 22°C and 60 % RH for 72 hours before use.

Single cigarette, total collection device

The equipment and methods used for the collection and the quantification of SS have been described previously (13). The smoking of the cigarette while enclosed in the collection device is almost identical to draft-free, open air smoking. This was assured by measuring static burn rate, mainstream smoke (MS) yields and coal temperature, and by computing air velocities inside the device (13). SS is collected as early as possible. Particulate matter is trapped on a Cambridge filter placed where the temperature of the incoming smoke is within 2 °C of ambient. Deposition inside the device is taken into account. The filter-load contents in water and nicotine are subtracted in order to approach the ETS situation more closely. Analytical procedures are very close to those employed in similar studies (14).

Experimental chamber

The equipment and the methods used for the analysis of aging SS in an air-

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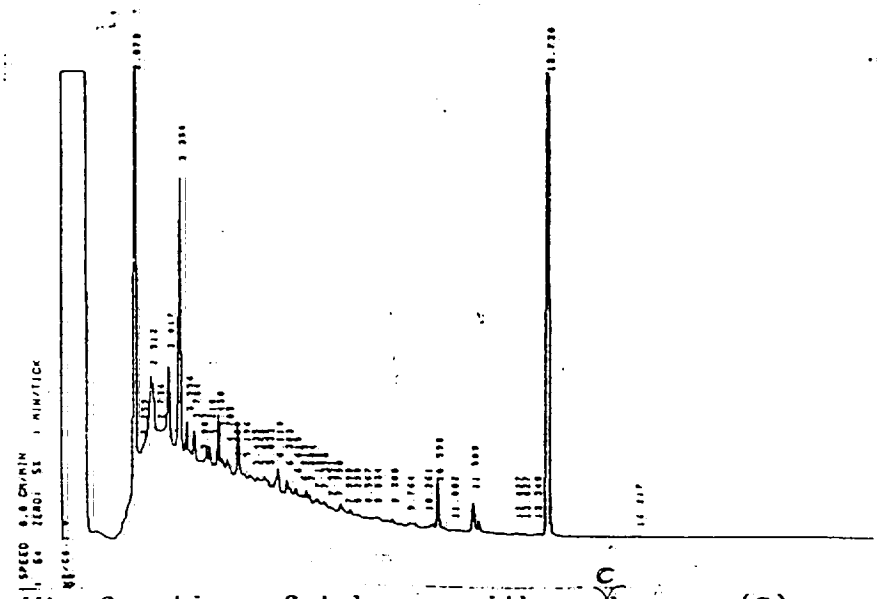
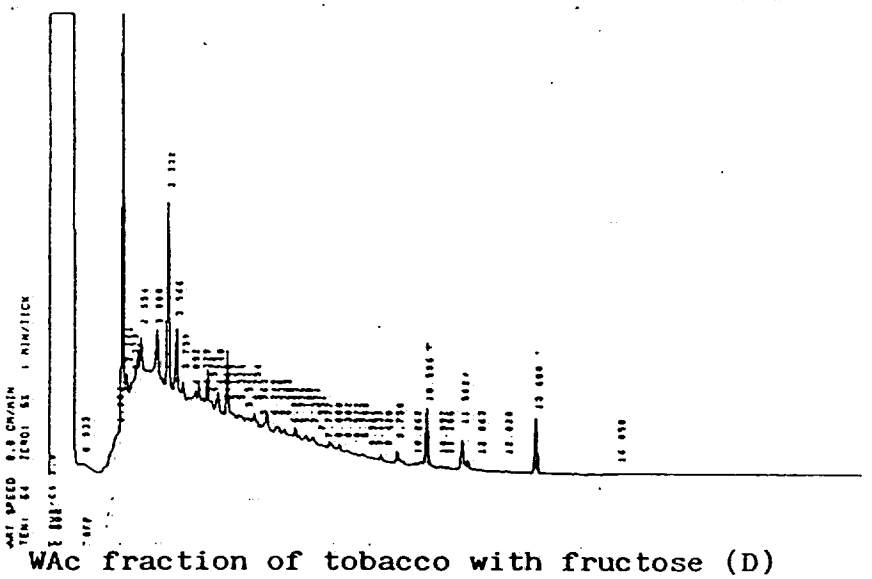
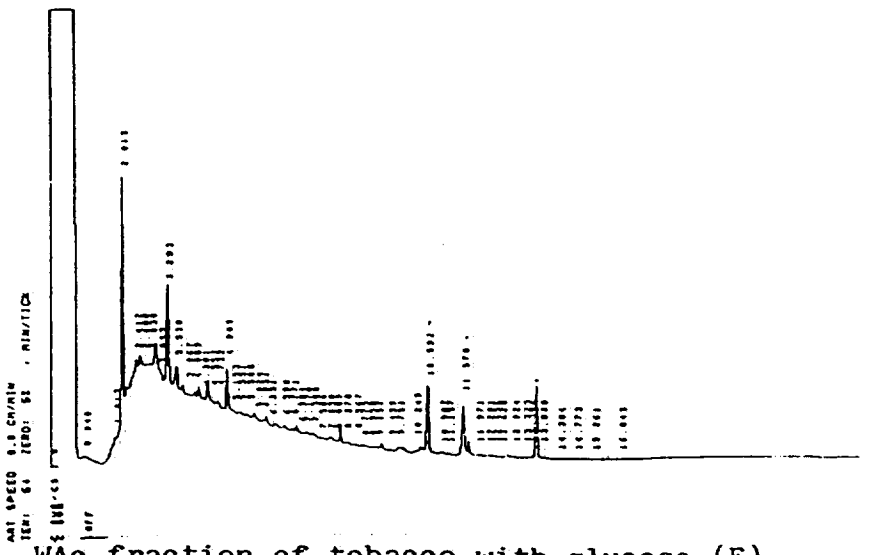


WAc fraction of tobacco with sacharose (C)



WAc fraction of tobacco with fructose (D)



WAc fraction of tobacco with glucose (E)

Fig 2: GC of WAc fractions

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TABLE 2 : Experimental design parameters

#	Samples	: 3
#	Ports/smoking run	: 4
#	Smoking processes/smoking run	: 3
#	Cigarettes/port	: 3
#	Cigarettes/smoking run	: 12
#	Smoking runs/day	: 3
#	Cigarettes/sample	: 36
#	Days/location	: 3

Smoking schedule

Day	1	2	3
Run		Sample	
1	DAC	1R4F	AB
2	AB	DAC	1R4F
3	1R4F	AB	DAC

The experimental design parameters are shown in Table 2. 36 cigarettes were smoked per sample over three days as shown by the smoking run schedule that appears in the figure. CORESTA 10 was followed for the basic smoking specifications. A flow rate of 3.0 litres per minute was used for sidestream collection in Madrid and Sevilla. Additionally, a 3.5 litre per minute flow rate was also used in Madrid in order to bring the yields obtained in Madrid into line with the ones in Sevilla.

The cigarettes were lit using a gas lighter, and immediately the chimneys were lowered and the plates set in a horizontal position. As soon as the coal reached the butt length, the cigarettes were extinguished using water.

CORESTA 7 and 8 were followed for the analyses of nicotine and water in condensate collected by sidestream and mainstream filters. The chimneys were washed using 100 cm3 of solvent (2-propanol containing 0.1 mg/cm3 of quinaldine as internal standard). These solutions were analyzed using a gas-chromatographic method (column 25 m, 20 M Carbowax, 530 µm ; injector 250° C; nitrogen-phosphorus detector, 250° C; oven 170° C; carrier flow 15 cm3/min.) suitable for low nicotine concentrations. All chromatographic analyses were performed exactly one week after smoking at the C.I.D. facilities in Madrid. Blanks and standards were prepared for each smoking day.

The carbon monoxide-carbon dioxide analyzer was calibrated using standard carbon oxide/nitrogen mixtures of 0.1 and 0.2 % CO for sidestream, 2 and 5% CO for mainstream, 0.5 and 1 % CO2 for sidestream and 5 and 10 % CO2 for mainstream. Gas-phase analyses were performed just after finishing each smoking process, for sidestream, and immediately after each smoking run, for mainstream.

The nicotine-free dry condensate (PMWNF) deposited in chimneys was estimated using the tar/nicotine ratio method.

RESULTS AND DISCUSSION

A prior statistical treatment of results consisting of Dixon outlyer tests

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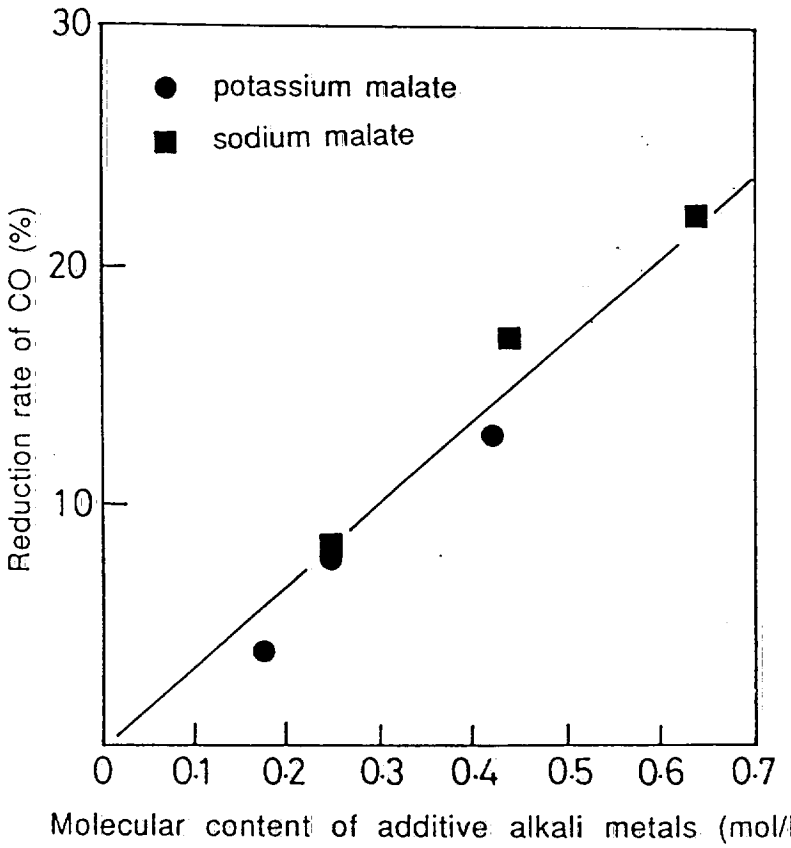
RESULTS

The effects of the molecular content of additive alkali metals on the reduction rate of CO in the mainstream smoke are shown in Fig. 1. The reduction rate of CO was linearly proportional to the molecular content of additive alkali metals.

FIG. 1
EFFECTS OF MOLECULAR CONTENT OF ALKALI METALS ON REDUCTION RATE OF CARBON MONOXIDE (FRACTIONAL VOLUME 0.32)



DTG curves are shown in Fig. 2 . In an atmosphere of nitrogen, the DTG curves were very similar regardless of the additive alkali metals, while in an atmosphere of air, the alkali metal salts affected the DTG curves significantly. As shown in Table 1, the amount of residue at 400°C in air was independent of the additive alkali metal salts. On the other hand, the amount of residue of tobacco with additives at 600°C in air was greater than that of the control tobacco. This indicates that the addition of the alkali metal had an effect on the oxidation of the char.

The DSC curves obtained from Sample A (a mixture of untreated tobacco char and K_2CO_3) were not influenced by the amounts of additives (Fig. 3). On the other hand, the first peak was absent from the DSC curves obtained from Sample B (char made from tobacco treated with potassium malate) (Fig.4). Therefore, it can be said that the addition of alkali metal salts affected the process of carbonization, but had no direct effect on the oxidation of chars.

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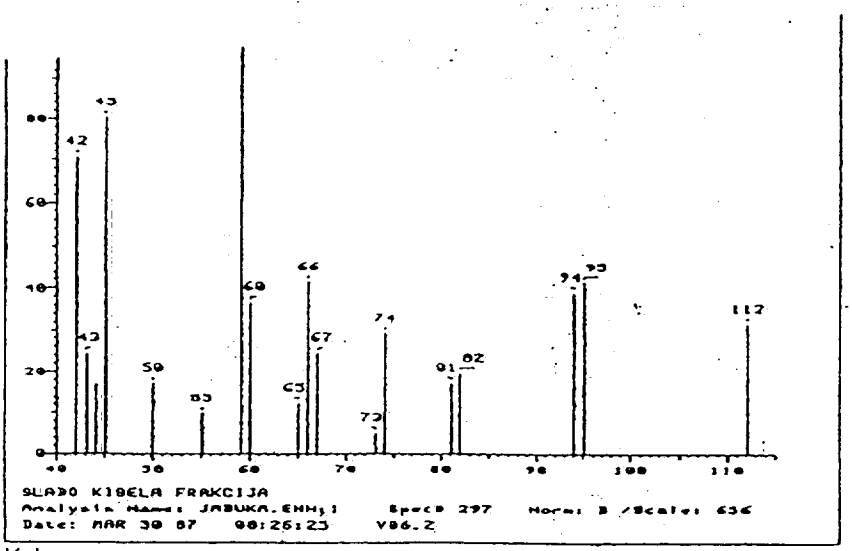

Fig. 4

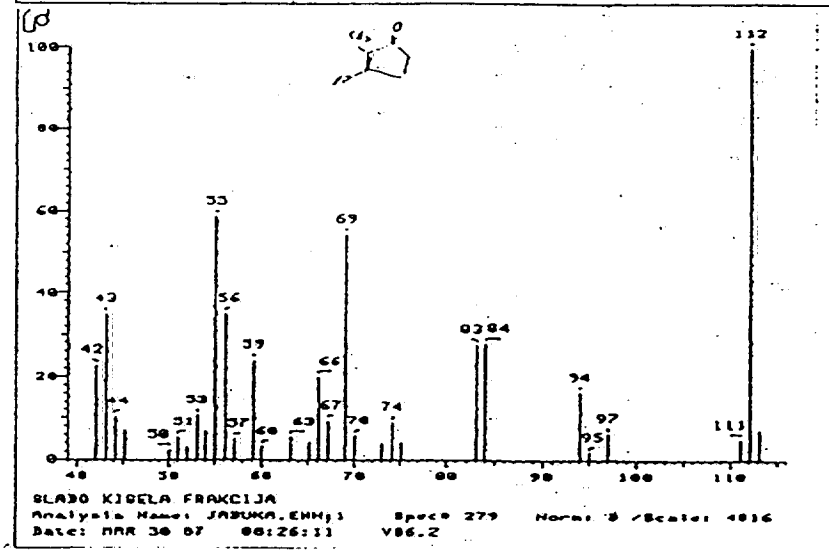

Fig. 5

The formation of a hexagon ring and further transformation into phenoles is proven, not only by increase in phenol of 10 %, but also by identification of 3-methyl-4,4-dimethyl-2-cyclohexene-1-one (Fig. 6).

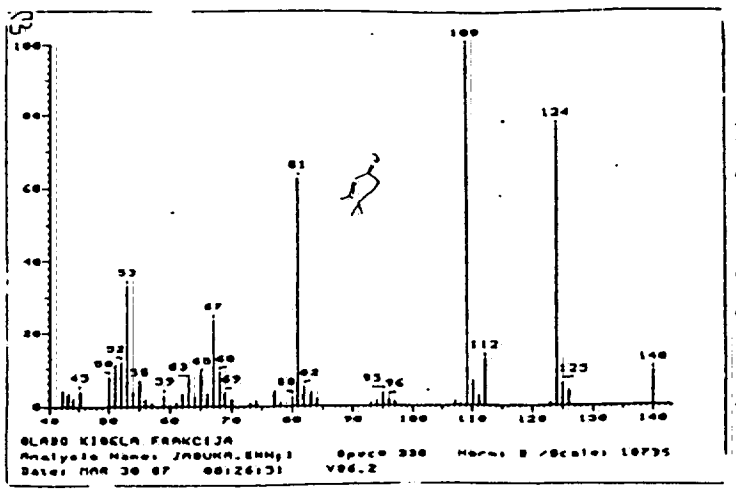

Fig. 6
These compound is, by structure, the same as compound 5 in Fig. 1. The compound was not identified in pure tobacco.

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The objective of this research was to determine whether sorbitol added to the tobacco mixture causes changes in the tar, nicotine and carbon monoxide yields of cigarettes made of Croatian tobaccos.

MATERIALS AND METHODS

The investigations were carried out on an experimental tobacco blend prepared in the laboratory. The blend was made up of tobaccos grown in Croatia and consisted of 70% Virginia and 30% Burley of different grades and leaf groupings.

The tobacco was cut on a laboratory cutting machine. The cutting width was 0.8 millimeters.

The tobacco blend was treated with a 70% sorbitol water solution produced by the firm PLIVA, Zagreb. The sorbitol was applied by spraying. Tobacco blend samples were prepared containing 1%, 3% and 5% sorbitol, as well as a sample without sorbitol which was used as a control.

The chemical properties of the tobacco blend samples were determined by conventional methods of analysis.

Experimental filter cigarettes were hand made from the tobacco blend samples. The cigarettes were prepared using 800 milligrams of the tobacco blend.

Machine smoking of the experimental cigarettes was carried out on a RM 20/CS smoking machine made by the firm Heinrich Borgwaldt. The smoke condensate was trapped on a Cambridge filter. Determination of crude and dry smoke condensate, determination of the nicotine content in the smoke condensate and determination of the carbon monoxide content in the mainstream smoke of cigarettes were carried out according to CORESTA Standard and Recommended Methods.

RESULTS AND DISCUSSION

The chemical properties of the tobacco blend used to prepare the experimental cigarettes, with and without sorbitol, are presented in Table 1.

TABLE 1
CHEMICAL CHARACTERISTICS OF THE TOBACCO BLEND

SORBITOL %	NICOTINE %	PROTEIN N %	TOTAL N %	REDUCING SUGARS %	TOTAL SUGARS %
0	2.39	0.9	2.12	13.31	16.62
1	2.37	0.88	2.13	13.24	16.23
3	2.41	0.89	2.11	13.66	16.56
5	2.38	0.87	2.09	13.68	16.91

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Some earlier investigations showed that sorbitol is suitable for conditioning Yugoslav tobaccos (1-4), that it has a certain fungistatic effect (5) and that its various properties make it suitable for use as a tobacco additive (6).

The results obtained indicate that sorbitol does not, in any of the concentrations investigated (1%, 3% and 5%), have a significant effect on the tar level, the nicotine content in the smoke condensate or the carbon monoxide content in the gas phase of the smoke of cigarettes prepared from the tobaccos used in this experiment. It may therefore be concluded that, with regard to cigarette smoke yields, sorbitol may be used in the above mentioned concentrations in the manufacture of cigarettes made from tobacco blends similar to those used in this research.

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5. H. Smit. Die Wirkung einiger Feuchthaltemittel auf die Eigenschaften eines roehrengetrockneten Tabaks. Beitr. Tabakforsch., 1970, 5, 231-238.

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isopropylmalonate and 4-diethylaminobutan-2-one methiodide were used as starting material. Considering the difficulty to separate the condensation product, ethyl 2-ethoxycarbonyl-2-isopropyl-5-oxohexanoate, by distillation, saponification and decarboxylation were completed without separation of the condensation product in this study. 2-Methyl-and 2-ethyl-5-oxohexanoic acid were synthesised with the same method. Methyl and ethyl esters of these three acids were prepared by direct esterification.

The effect of these compounds on cigarette smoke were evaluated.

EXPERIMENTAL

DIETHYL METHYLMALONATE To a stirred mixture of dimethyl sulphate (73.2g), diethyl malonate (80g), tetrabutylammonium iodide (8.1g) and benzene (300ml), cooled to 10℃, a solution of 44% sodium hydroxide in water was added and the temperature was kept at 15~20℃. Having stirred at the same temperature for 45 min, 100ml of water were added to the mixture. The organic layer was separated and washed with water to pH7. After removal of benzene by distillation, diethyl methylmalonate (79g, 91.9% yield) was collected at 70~73℃/5mmHg, n_D^{32} 1.4067 (n_D^{20} 1.4226 in reference [26]).

Diethyl ethylmalonate and diethyl isopropylmalonate were prepared according to the method described in the reference [27].

4-DIETHYLAMINOBUTAN-2-ONE A mixture of acetone (500ml), formaldehyde (120g, 36% solution in water) and diethylamine hydrochloride (154g) was refluxed for 12 hrs. About 350ml of acetone were distilled off and a solution of 56g of sodium hydroxide in 210ml of water was added to the residue. The upper organic layer was separated and the water layer was repeatedly extracted with ethyl ether. The combined organic layer were dried over anhydrous potassium carbonate. After evaporation of ethyl ether and acetone, vacuum distillation of the residue gave 4-diethylaminobutan-2-one (155.7g) which was collected at 70~73℃/15mmHg, n_D^{21} 1.4348 (bp 84℃/30mmHg and n_D^{24} 1.4333 in reference [26]).

4-DIETHYLAMINOBUTAN-2-ONE METHIODIDE IN ETHANOL To a stirred solution of 4-diethylaminobutan-2-one (28.6g) in 30ml ethyl ether, methyl iodide (40g) in 10ml of ethyl ether was added below 5℃. The turbid mixture obtained was

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This tendency was in accordance with the yield of carbonaceous residue obtained from by heating with the electric furnace for the DSC measurement (Table 3).

When alkali metals were added on tobacco, the maximum temperature of solid phase during puffing was lowered (Table 4).

TABLE 2
THE AMOUNT OF OXYGEN CONSUMED DURING PUFFING, THE WEIGHT OF CARBON IN CONE AND ASH, AND YIELDS OF TOBACCO CHAR (FRACTIONAL VOLUME 0.32)

Additive	Molecular content mol/kg	Oxygen consumed ml/cig.	Weight of carbon in cone mg/cone	Weight of carbon in ash mg/cig.	Yield of tobacco char %
Control	0	26.0	8.9	3.2	27.3
Potassium malate	0.18	25.6	9.8	3.4	27.7
	0.25	24.2	9.6	3.7	28.3
	0.42	23.8	9.8	3.8	26.7
Sodium malate	0.25	25.2	9.1	4.6	27.4
	0.44	24.2	8.9	5.9	31.0
	0.64	24.0	8.7	6.3	27.5

TABLE 3
YIELDS OF CHAR (SAMPLE B: CHAR MADE FROM TOBACCO TREATED WITH POTASSIUM MALATE USING AN ELECTRIC FURNACE)

Additive	Molecular content mol/kg	Yields of tobacco char %
Control	-	27.8
Potassium malate	0.18	28.2
	0.33	30.4
	0.76	28.8

TABLE 4
THE MAXIMUM TEMPERATURE OF SOLID PHASE DURING PUFFING (FRACTIONAL VOLUME 0.31)

Cigarette	Additive content mol/kg	Maximum temperature of solid phase °C	
Control	-	801	(n=50)
Potassium additive	0.42	781	(n=65)
Sodium additive	0.64	731	(n=34)

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LA NICOTINE DANS LA FUMÉE. PAR RAPPORT AUX CONDITIONS LIMITEURS DES LIMITES ÉTAIENT ADOPTÉES POUR LES DIFFÉRENTS COMPOSANTS DU MÉLANGE, QUI NE CONDUIRAIENT PAS AUX MODIFICATIONS DES PROPRIÉTÉS CARACTÉRISTIQUES À LA MARQUE. CELA ÉTAIT CONFIRMÉ PAR L'ÉVALUATION DE DÉGUSTATION DES CIGARETTES À MÉLANGE EXPÉRIMENTAL. L'INFLUENCE DE LA COMPOSITION MODIFIÉE DU MÉLANGE SE TRADUIT PAR UNE RÉDUCTION DES GOUDRONS DE 3,09 MG/CIG. (9.97%), DE LA NICOTINE PAR 0,06 MG/CIG.(4.20%) ET DU MONOXIDE DE CARBON PAR 1.27 MG/CIG. (5.78%).

LES DONNÉES MONTRENT QU'IL N'Y A PAS DE DIFFÉRENCES SIGNIFICATIVES ENTRE LES RÉTENTIONS DES DEUX FILTRES ÉTUDIÉS CAR LES DIFFÉRENCES SONT BIEN DANS LES LIMITES DE PRÉCISION DES MÉTHODES ANALYTIQUES.

BIEN QUE LE POIDS DES CIGARETTES DIMINUE LORSQU'ON UTILISE DES CÔTES EXPANSÉES, IL N'Y A PAS D'INFLUENCE PERCEPTIBLE SUR LA CONCENTRATION DES SUBSTANCES ÉTUDIÉES.

TOUTES LES SUBSTANCES ÉTUDIÉES DE LA FUMÉE (GOUDRONS, NICOTINE ET MONOXIDE DE CARBON) DIMINUENT SOUS L'INFLUENCE DE L'ADDITIF.LA RÉDUCTION DES GOUDRONS EST LA PLUS IMPORTANTE ET ATTEINT 3,16 MG/CIG. (11.01%) AVEC LE FILTRE 3/32.000 D.P.F. ET AVEC DES CÔTES EXPANSÉES. LA RÉDUCTION MAXIMALE DE LA NICOTINE EST 0,09 MG/CIG. (6.62%) ET CELLE DU MONOXIDE DE CARBON - 6.80 MG/CIG. (27.62%). L'EFFET DE CET ADDITIF EST SANS DOUTE POSITIF, CAR LA RÉDUCTION EST OBSERVÉE DANS TOUS LES TRAITEMENTS (CIGARETTES ESSAI).

L'INFLUENCE COMPLEXE EST ÉTUDIÉE PAR RAPPORT AU DEUX TÉMOINS (TABLEAU 2). TÉMOIN I REFLÈTE L'INFLUENCE DE TOUS LES FACTEURS - TABACS, EXPANSION DES CÔTES, USAGE D'ADDITIF ET FILTRE. UNE RÉDUCTION IMPORTANTE EST CONSTATÉE: LES GOUDRONS SONT RÉDUITS PAR 5,79 MG/CIG. (18.57%) AVEC LE FILTRE 3/35.000 ET PAR 6,94 MG/CIG. (22.58%) AVEC LE FILTRE 3/32.000 D.P.F.;LA NICOTINE EST RÉDUITE RESPECTIVEMENT PAR 0,16 MG/CIG. (11.19%) ET PAR 0,13 MG/CIG. (9.10%); LE MONOXIDE DE CARBON EST RÉDUIT RESPECTIVEMENT PAR 6,79 MG/CIG. (30.88%) ET 3,18 MG/CIG.(14,46%).

LE TÉMOIN II REFLÈTE L'INFLUENCE COMBINÉE DES AUTRES FACTEURS - ADDITIF, CÔTES EXPANSÉES ET FILTRE. DANS CE CAS L'EFFET EST MOINS SIGNIFICATIF.

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the development of new production processes within the industry has also played an important role in the reduction of the level of smoke constituents.

The mutual interdependence of brand and production development has always been strong, but today it is even stronger. The production development has been considerably influenced by the beginning of the production of foreign licensed products from the 1970's.

At the moment the Hungarian tobacco industry produces more than 1.3 billions of licensed cigarettes, which is 5 % of the total Hungarian consumption. With the growth of the production of licensed cigarettes not only the demand for the improvement of cigarette makers and packing machines has increased but also that of tobacco cutting machines and the processing technology. As a result of these improvements the amount of tobacco filled in the cigarettes decreased which, naturally, also meant a reduction in the smoke delivery of cigarettes.

The greatest change introduced into the processes preparatory to cigarette production was the employment of the "expansion technique" in the last few years. The equipment needed was imported, but now there is also a Hungarian machine in the test stage, which uses less energy and contains no moving parts. According to our experiences so far, the efficiency of expansion in the case of cut rolled stems is 30 to 35 %, while for rags it is 20 to 30 %, depending on the quality of the tobacco.

The decrease in the amount of tobacco used is well illustrated by the fact that at the moment there is ca. 6 % less tobacco in the cigarettes than there used to be in 1985. The ongoing automation of processing, especially the regulation of the massflow, may also lead to the decrease of the amount of tobacco needed. Technical improvement has begun in this field as well, partly based on Hungarian results of research.

The turning of processing waste into reconstituted sheet has become important in both economic and sanitary respects. The technology of producting reconstituted sheet is being modernised.

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ROLE OF ALKALI METALS IN REDUCTION OF CARBON MONOXIDE IN MAINSTREAM SMOKE

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SUMMARY

The formation rate of CO in mainstream smoke has been reported to be dependent on the potassium content in tobacco. This work was undertaken to elucidate the role of alkali metals in CO reduction. CO in cigarette smoke has been shown to be produced by three processes; thermal decomposition of the tobacco constituents, combustion of the tobacco constituents, or carbonaceous reduction of CO_2. In this paper, the contribution of alkali metals to each process of CO formation is discussed.

The DSC curve of tobacco char in air is made up of 2 peaks. In the case of the carbonaceous residue of tobacco treated with alkali metal salts, the first peak of the DSC curve, which is attributable to the oxidation of the more reactive portion of char, disappeared and the surface area of char decreased. However, the DSC curves obtained from a mixture of untreated tobacco char and alkali metal salts were not influenced by the amount of the salts. Accordingly, it is considered that alkali metal salts caused a more stable char to form during the decomposition process of tobacco. Also, the amount of oxygen consumed during the puff decreased, and the maximum temperature of the solid phase of the burning cone during the puff was lowered when alkali metals were added to the cigarette.

Consequently, the amount of CO formed in the combustion process was reduced by alkali metal salts. Moreover, the temperature of the burning cone was lowered, and the CO formed from carbonaceous reduction decreased.

INTRODUCTION

Decreasing the level of CO in mainstream smoke is important in cigarette manufacture. The formation rate of CO has been reported to be dependent mainly on the potassium content of tobacco (1,2). CO in cigarette smoke has been shown to be produced by three processes; namely, thermal decomposition of tobacco constituents, combustion of tobacco constituents, and carbonaceous reduction of CO_2. Each process produces about one third of the total quantity of CO formed in mainstream smoke (3). In this paper, the contribution of alkali metals to CO formation from each process is discussed.

In a previous paper (1), we discussed the idea that the temperature of the burning zone fell with the increase in potassium content of tobacco shreds, resulting in the decrease of CO formation via CO_2. However, alkali metal salts are used as accelerating catalysts for gasification of carbon black and coal, that is as accelerating catalysts for carbonaceous reduction of CO_2, and many studies on this mechanism have appeared (4). Therefore, we now

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and smoke flavour. Many papers have been published concerning the analysis of low-molecular weight carbohydrates in tobacco leaf and in cigarette filler(1).
Some authors determine the total reducing sugars with colorimetric methods, others describe gas-chromatographic procedures using the trimethylsilyl derivatives or estimate the individual compounds by paper and thin layer chromatography(2-4).
Battard J.C. and Chauvett C. used the high performance liquid chromatography for rapid characterization of tobacco sugars(5).
The purpose of this work is to find the best conditions for detecting and determining as large a number as possible of both reducing and non reducing low-mulecular weight carbohydrates present in standard mixtures and to apply such conditions to the analyses of tobacco leaf and cigarette filler by the aid of the High Performance Ion Chromatography with pulsed amperometric detection.

EXPERIMENTAL

REAGENTS

The twenty-five carbohydrates (Merck for biochemistry) reported in table 2 were used without further purification to prepare the standard solutions, using distilled and purified in an ELGASTAT system water.
These solutions were kept at 4°C and were found to be stable for at least 15 days.
Solutions of 0.2N and 1.0N NaOH (Merck or Fluka reagent grade) were used.
All eluent solutions were prepared by bubbling helium at first through the water to prevent the carbon dioxide contamination, and were kept under a blanket of helium during elution.

APPARATUS AND PROCEDURES

A DIONEX BIO-LC Chromatograph equipped with:
- a gradient pump module, operating up to 4000 p.s.i.;
- a Dionex Eluent Degas Module with Eluant Container set;
- a Pulsed Amperometric Detector (PAD-2) containing a working gold electrod;
- a sample injection valve with a 50µl sample loop;
- a Dionex DQP-1 post column pumping sistem;
- ON-GUARD RP filters;
- HPIC-AS6 column with amino modified polystirene-divinylbenzene phase (250x4mm, 10µm particle size bed) protected by a guard column HPIC-AG6 (70x4mm);
- HPIC-AS6A column (150x4mm) with amino modified polystirene-divinylbenzene phase, 5µm particle size bed, protected by a guard column HPIC-AG6A (50x4mm);
- a Varian 1200 recorder.

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- UTILISATION DE CÔTES:	3. CÔTES EXPANSÉES.
	4. CÔTES NON EXPANSÉES.
-ADDITIFS AU TABAC:	5. SANS ADDITIF.
	6. AVEC ADDITIF.
- FILTRES À CIGARETTES:	7. 3,9/35.000 D.P.F.
	8. 3/35.000 D.P.F.
	9. 3/32.000 D.P.F.

LE MÊME PAPIER À CIGARETTES À PERMÉABILITÉ 24 UNITÉS CORESTA (CM/MIN 10 CM H_2O) ÉTAIT UTILISÉ POUR TOUTES LES CIGARETTES.

LE MÉLANGE EXPÉRIMENTAL EST PRÉPARÉ À L'AIDE D'UN MODÈLE D'OPTIMISATION À BASE DE PROGRAMMATION LINÉAIRE. LES CÔTES COUPÉES SONT EXPANSÉES PAR LA MÉTHODE "HT" JUSQU'À 20% ET UTILISÉES À 10% DANS LA COMPOSITION DU MÉLANGE. L'ADDITIF EST UTILISÉ À 1% DE LA MASSE DE TABAC. LES FILTRES SONT 90 MM LONGS À DIAMÈTRE 7.85MM, À POIDS ET RÉSISTANCE AU TIRAGE OPTIMUMS.

DEUX TÉMOINS ÉTAIENT UTILISÉS: TÉMOIN I EST LA CIGARETTE À MÉLANGE STANDARD AVEC FILTRE DE 3,9/35.000 D.P.F.; TÉMOIN II EST LA CIGARETTE À MÉLANGE ESSAI AVEC FILTRE DE 3/35.000 D.P.F.

LES GOUDRONS, LA NICOTINE ET LE MONOXIDE DE CARBON ÉTAIENT DÉTERMINÉS SUIVANT LES MÉTHODES DU CORESTA. LES CIGARETTES STANDARD ÉTAIENT COMPARÉES À CHAQUE TRAITEMENT DES CIGARETTES ESSAI DANS UNE ÉVALUATION D'EXPERTS EN DÉGUSTATION PAR LA MÉTHODE DES "PAIRS" (DIFFÉRENCES).

RESULTATS ET DISCUSSION

LES RÉSULTATS POUR LE CONTENU DES SUBSTANCES ÉTUDIÉES DANS LES DIFFÉRENTS TRAITEMENTS SONT PRÉSENTÉS DANS LE TABLEAU 1.

CHAQUE COMBINAISON (TRAITEMENT) DE LA CIGARETTE DIFFÈRE DE LA PRÉCÉDENTE PAR UN OU DEUX ÉLÉMENTS. CES COMBINAISONS PERMETTENT D'ÉTUDIER L'INFLUENCE DE CHAQUE FACTEUR SÉPARÉMENT, AINSI QUE L'INFLUENCE COMPLEXE DE TOUS LES FACTEURS SUR LES INDICES ÉTUDIÉS DE LA FUMÉE.

COMME INDIQUÉ CI-DESSUS LA COMPOSITION MODIFIÉE (EXPÉRIMENTALE) DU MÉLANGE ÉTAIT PRÉPARÉE PAR UN MODÈLE D'OPTIMISATION EN RÉDUISANT AU MINIMUM LA CONCENTRATION DES GOUDRONS ET DE

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stirred below 5℃ for 30 min. and then at room temperature for 1 hr. After removing ethyl ether and unreacted methyl iodide by filtration, a white solid was obtained and then dissolved in 100ml of absolute ethanol for next step use.

2-ALKYL-5-OXOHEXANOIC ACID Diethyl alkylmalonate (0.2mol) was added to a solution of 4.6g of sodium in 150ml of absolute ethanol, the mixture was refluxed with stirring for 5 min. To the mixture, cooled in ice-salt, the above prepared solution of 4-diethylaminobutan-2-one methiodide in absolute ethanol was gradually introduced. After stirring at 0-5℃ for 5 hrs., the mixture was kept at room temperature overnight and followed by reflux for 4 hrs. About 120ml of ethanol were distilled off, the residue was refluxed with 30g of potassium hydroxide in 24ml of water for 1 hr., then the mixture was diluted with 60ml of water. Distilling off the ethanol as completely as possible, the alkaline residue was acidified to pH3 with dilute hydrochloric acid and extracted repeatedly with ethyl ether. After removal of the ethyl ether by distillation the reidue was heated at 130-140℃ until evolution of carbon dioxide ceased. Vacuum distillation of the residue gave 2-alkyl-5-oxohexanoic acid.

2-Methyl-5-oxohexanoic acid (12.4g) was collected at 130-140℃/3~4mmHg (IR: 3180-3020, 2937, 1720, 1462, 1416, 1376, 1166, 1124, 808, 741; MS: 127, 101, 99, 87, 73, 71, 57, 43).

2-Ethyl-5-oxohexanoic acid (10.5g) was collected at 126-134℃/2mmHg (IR: 3160-3018, 2967, 1725, 1462, 1416, 1360, 1227, 1167, 1100, 945, 780; MS: 158(MW), 141, 140, 115, 113, 101, 87, 71, 70, 57, 56, 45, 43, 42).

2-Isopropyl-5-oxohexanoic acid (15.3g) was collected at 128-136℃/2mmHg (IR: 3100-3010, 2965, 2937, 1723, 1468, 1417, 1390, 1370, 1230, 1165, 935, 848; MS: 172(MW), 155, 154, 127, 111, 101, 97, 83, 71, 58, 56, 43).

METHYL AND ETHYL ESTERS OF 2-ALKYL-5-OXOHEXANOIC ACID The acid and methanol or ethanol were refluxed with concentrated sulphuric acid for 6 hrs. The mixture was dried and neutralized with anhydrous potassium carbonate. After removal of the alcohol the ester was obtained by vacuum distillation.

Methyl 2-methyl-5-oxohexanoate was collected at 75-78℃/3mmHg (IR:

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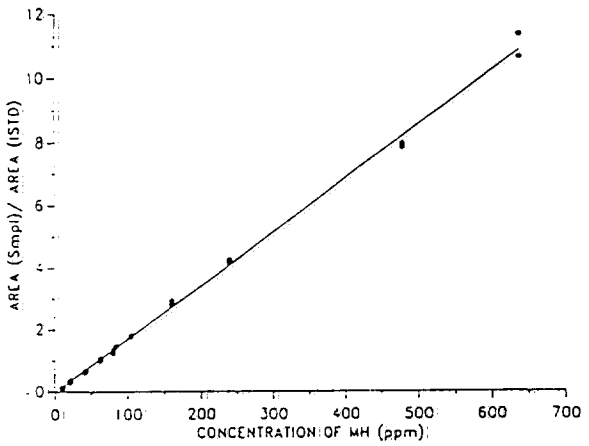

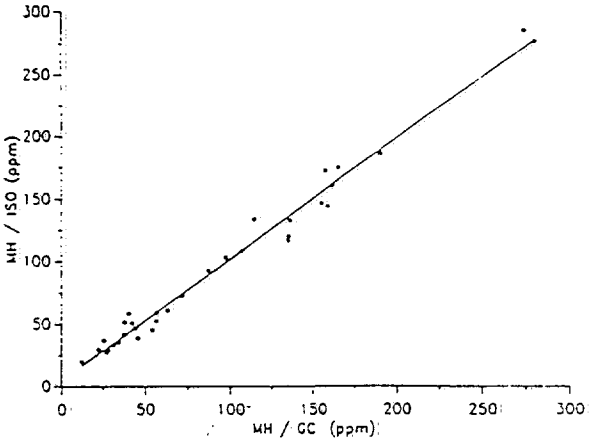

The bottleneck of the method is the hydrolysis step which is time-consuming and requires a lot of glassware. At present, the number of samples which can be processed everyday by one person is limited to 20. However, the daily capacity of the GC method is at least twice as high as the colorimetric one and could be increased greatly if, for example, the acid hydrolysis could be replaced by an enzymatic one.

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$KMnO_4$. All self synthesized substances were TLC purified and their identity was verified by MS (10).

(k) Test tobacco : oriental (Prilep) tobacco type.

Apparatus

(a) Ultra-Turrax (type 45).
(b) Rotatory vacuum exaporator.
(c) Basic TLC equipment.
(d) Thermostat.

Extraction

5 g dry powdered tobacco are extracted with 200 ml acetone for 5 minutes on Ultra-Turrax at moderate speed. The sample is filtered through Celite. A 50 ml aliquot is taken and vacuum evaporated to about 1 ml.

Oxidation and clean-up

To the residue in the flask 25 ml of oxidant is added. The reaction mixture is heated to about 35°C and magnetically stirred for 20 minutes. The oxidation is followed by addition of saturated aqueous solution of Na_2SO_3 until the violet colour disappears. The sample is transferred to a separating funnel, 20 ml of n-hexane are added and shaken about 1 minute. The water extract is retained. The n-hexane phase is re-extracted with 20 ml water and the water phase added to the first water extract. The oxon sulfones are extracted from water solution into dichloromethane (3X 20 ml). Finally, the dichloromethane extract is washed once with 25 ml water (for elimination of residues of acetic acid). The dichloromethane extract is filtered through Na_2SO_4 anhydrous and vacuum evaporated at room temperature to appropriate volume (for samples with unknown concentration to 10 ml).

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For the determination of total MH, i.e., free and glucosidic, an acidic digestion precedes the reduction with Zn. The colorimetric method has several drawbacks : interferences from several leaf constituents are possible [5]; the procedure is time-consuming and relatively difficult to handle. Therefore, a specific and more simple procedure is needed for MH determination on tobacco. This paper describes a method using acidic hydrolysis, methylation and gas chromatography with a Nitrogen-Phosphorous detector for the quantitative and unambiguous determination of MH on tobacco.

EXPERIMENTAL SECTION

Apparatus

Gas chromatograph, Carlo Erba 5160 equipped with Nitrogen-Phosphorous detector (NPD) and connected to a Spectra-Physics DP-700 integrator.

GC column, 30 m x 0.25 mm i.d. fused silica column, coated with 0.25 um of DB-17, J&W.

Gas chromatograph - mass spectrometer, Hewlett Packard 5988 mass spectrometer, interfaced with a Hewlett Packard 59970 data system and a Hewlett Packard 5890 gas chromatograph.

NMR spectrometer, Bruker WP-200

Reagents

- Maleic hydrazide (MH) 99 %, Riedel-de-Haën
- 5.5-dimethylbarbituric acid (barbital), puriss p.a., Fluka
- Hydrochloric acid, puriss p.a., 32 %, Fluka
- Dimethyl sulfate, puriss p.a., Fluka
- Potassium carbonate, p.a., Merck
- Sodium hydroxyde, puriss p.a., Fluka
- Chloroform, puriss p.a., Fluka
- Extracting solution : barbital in 2N hydrochloric acid, 1 mg/l
- Calibration solution : maleic hydrazide in extracting solution, 1 mg/l.

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- the first Hungarian low nicotine cigarette - and its most recent development.

This "White Helikon" also proves that our newest products belong to what is called the "low tar" category, even according to international standards.

TABLE 4

MAINSTREAM SMOKE COMPONENTS OF HELIKON CIGARETTE BRANDS IN 1989

BRAND	TAR mg/cig.	NICOTINE mg/cig.	CO mg/cig.
Helikon	18,6	0,86	17,5
Helikon white	11,5	0,55	10,7

Unfortunately, the share of these products on the market is still low today, just a few percent. Today, the greatest hindrance in the way of introducing these new products, which are lower in smoke constituents, is the misconstrued prohibition of advertisement. A much more favourable and comforting state could be achieved by purposeful advertisement. Because of the low share of these new products on the market, the mean values of the main smoke components decrease only to a little extent in the average Hungarian consumption, especially the CO content.

Keeping the interests of the smokers in mind, it would be very useful if sanitary inspectors would not only prohibit, at last, but would take into consideration the interrelationship between the various social, economic and sanitary factors.

These factors exist, even if we do not want to know about them. It is also undoubtable that it is the basic right of every human being to know what one gets for one's money.

Those who satisfy existing social demands should enjoy competition neutrality in order to have developmental opportunities which serve decent purposes. And all this is impossible without informationor informative advertisement !

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ETUDE DE L'EFFET DE CERTAINS FACTEURS SUR LA COMPOSITION DE LA FUMEE DE CIGARETTES

SVETOZAR GUEORGUIEV, DIMITAR GUENTCHEV, ALEXANDRE TOMOV, VALENTINE MINEV, NICOLAS YORDANOV

RÉSUMÉ

LA RÉDUCTION TOTALE DES SUBSTANCES DANS LA FUMÉE DE TABAC DÉPEND DE L'ACTION COMBINÉE D'UN ENSEMBLE DE FACTEURS. EN OUTRE, LA RÉDUCTION TOTALE N'EST PAS UNE SOMME SIMPLE DES RÉDUCTIONS INDIVIDUELLES, RÉSULTANTES D L'EFFET DE CHAQUE FACTEUR. A CAUSE DE CELA, LA COMPOSITION DE LA FUMÉE NE PEUT ÊTRE ÉTABLIE QUE PAR VOIE EXPÉRIMENTALE.

CE TRAVAIL A EU POUR BUT D'ÉTUDIER LES POSSIBILITÉS DE RÉDUIRE LES GOUDRONS, LA NICOTINE ET LE MONOXIDE DE CARBON DANS LA FUMÉE DE CIGARETTES.

UNE MARQUE DE CIGARETTES ÉTAIT UTILISÉE, PRISE COMME STANDARD. NEUF TRAITEMENTS ÉTAIENT PRÉPARÉS. C'ÉTAIENT DES COMBINAISONS DE: DEUX DIFFERENTES COMPOSITION DU MÉLANGE (STANDARD ET EXPÉRIMENTAL), AVEC ET SANS CÔTES EXPANSÉES (10% DE CÔTES, EXPANSÉES À 20%), AVEC ET SANS AJOUT D'ADDITIFS AU TABAC (1% EN POIDS) ET TROIS FILTRES D'ACÉTATE DE DIFFÉRENTS DENIERS (3,9/35.000, 3/35.000 ET 3/32.000 D.P.F.).

LES GOUDRONS, LA NICOTINE ET LE MONOXIDE DE CARBON ÉTAIENT DÉTERMINÉS SUIVANT LES MÉTHODES DU CORESTA. LES CIGARETTES STANDARD ET CELLES DES DIFFÉRENTS TRAITEMENTS ÉTAIENT COMPARÉES DANS UNE ÉVALUATION D'EXPERTS EN DÉGUSTATION.

LES RÉSULTATS ONT MONTRÉ QU'IL EST POSSIBLE DE RÉDUIRE LES GOUDRONS DE 22,58%, LA NICOTINE DE 9,10% ET LEMONOXIDE DE CARBON DE 14,46%. LA PART RELATIVE LA PLUS IMPORTANTE DANS LA RÉDUCTON EST CELLE DU MÉLANGE (50% ENVIRON), SUIVIE PAR CELLE DE L'ADDITIF (40% ENVIRON). L'UTILISATION DE CÔTES EXPENSÉES NE RÉDUIT PRATIQUEMENT PAS LES SUBSTANCES DANS LA FUMÉE. IL N'Y A PAS DE DIFFÉRENCE SIGNIFICATIVE DANS L'ÉFFICACITÉ ENTRE LE FILTRE À 3/35.000 D.P.F. ET CELUI À 3/32.000 D.P.F., MAIS TOUS LES DEUX SONT PLUS ÉFFICACES QUE LE FILTRE À 3,9/35.000

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during the last few years. Consumption per head has reached and amount where we can talk about a saturation level.

The considerable price rises of the last few years have caused only short and temporary changes. These facts justify and support also from a social standpoint the main research target of the Hungarian tobacco industry to increase the consumer's choice in the low-tar cigarette segment.

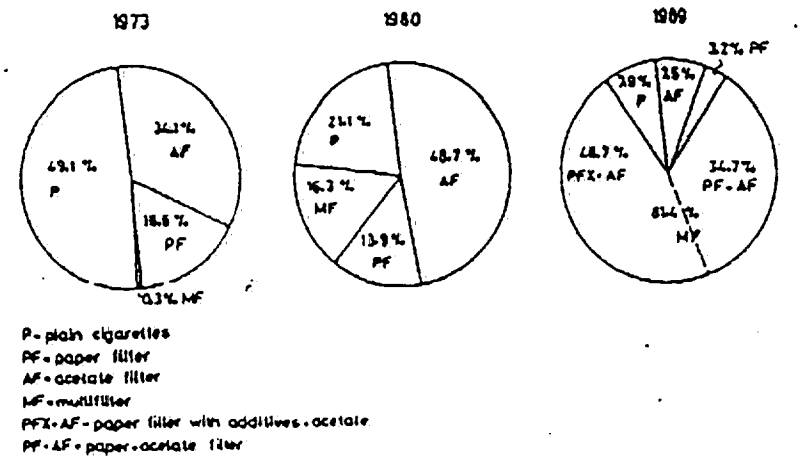
The first filter-tipped cigarette brand appeared in 1962 and was followed by more and more others as a result of a target-oriented development of new brands. How fast filter-tipped brands became universal is shown by the following facts. The rate of filter-tipped cigarettes in the market was more than 50 % at the end of the 1970's. This rate grew over 80 % in the 1980's. In 1989, 92,1 % of all cigarettes were filter-tipped.

The range of filter-tipped cigarettes was widened from the beginning of the 1970's by cigarettes with combined filters, which we call multi-filter tipped cigarettes. It is a special feature of the Hungarian cigarette market that the rate of cigarettes with multi-filters is rather high compared to other countries.

The second figure illustrates the change in cigarette consumption according to the type of filters. It was in 1973 that the first multi-filter tipped cigarette containing activated carbon appeared and proved to be a great success in the market later on.

Fig. 2

MARKET SHARE (%) OF CIGARETTES WITH DIFFERENT FILTER CONSTRUCTION IN HUNGARY



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SYNTHESIS OF 2-ALKYL-5-OXOHEXANOIC ACIDS AND ESTERS AND THEIR EFFECT ON CIGARETTE SMOKE

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SUMMARY

2-Isopropyl-5-oxohexanoic acid is a degradation product of cembranoids and an important component of the acidic fraction in Oriental tobacco. It produces the hay-like odor and gives slightly grassy smell to smoke. This study is aimed at sythesising a series of 2-alkyl-5-oxohexanoic acids and their esters and determining the effect of these compounds on cigarette smoke.

4-Diethylaminobutan-2-one is obtained by a modified Mannich reaction in yields of 70%. Methiodised 4-diethylaminobutan-2-one and diethyl malonates are submitted to a thermal-induced Michael addition reaction to synthesise the acids in one step.

It is found that 2-isopropyl-5-oxohexanoic acid and its esters have a noticeable effect in sensory tests. They enhance and improve the flavor of smoke and reduce the irritation of blended type cigarettes and contribute to flue-cured type cigarettes.

Meanwhile it is revealed that the isopropyl radical in C-2 of the acids play an important role in enhancing the flavor of cigarette smoke.

INTRODUCTION

2-Isopropyl-5-oxohexanoic acid is a terpenoid acid in the acidic fraction of Oriental [1-4], flue-cured [5-7] and burley [8] tobacco. The acid is a degradation product of cembranoids and has the characteristic aroma of Oriental tobacco [2,3].

Several methods in the synthesis of 2-isopropyl-5-oxohexanoic acid have been reported [9-25], With reference to Bardhan's method [24], diethyl

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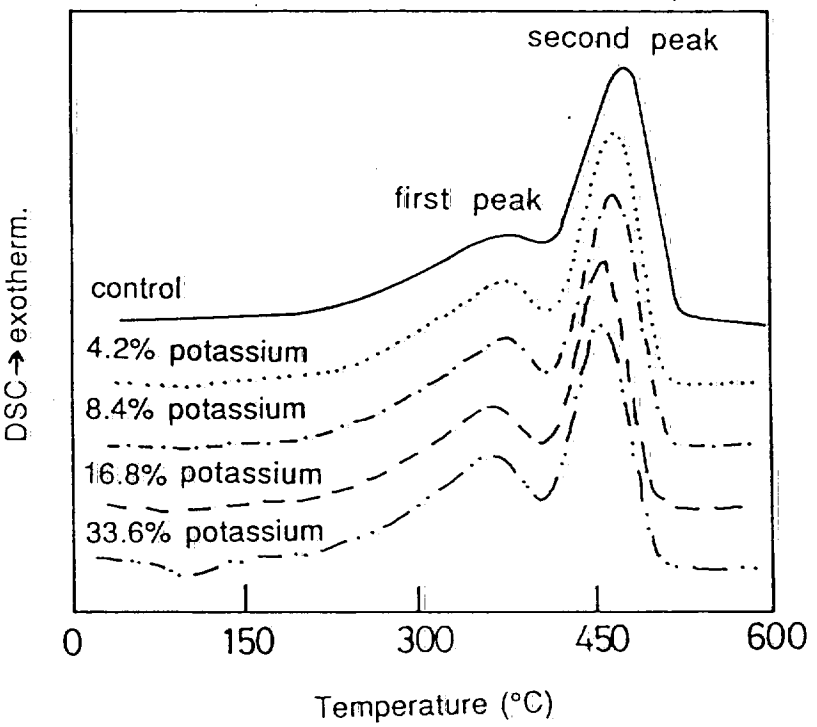
TABLE 1.
THE AMOUNT OF RESIDUE OF TOBACCO WITH AND WITHOUT ALKALI METAL SALTS BY THERMOGRAVIMETRY IN AN ATMOSPHERE OF AIR

Additive	Molecular content mol/kg	Amount of residue at 400°C %	at 600°C %
Control		37.4	8.6
Potassium malate	0.42	38.9	13.4
Sodium malate	0.64	39.3	13.8

FIG. 3
DSC CURVES OF SAMPLE A (MIXTURE OF UNTREATED TOBACCO CHAR AND K_2CO_3)



The surface area of char made from tobacco treated with potassium malate (Sample B) is shown in Fig. 5. The surface area is represented by the amounts of carbonaceous residue without additives. The surface area of chars decreased with increasing potassium content. These results support the idea that potassium in tobacco produces the more stable char during thermal decomposition of the tobacco constituents.

The apparent amount of oxygen consumed during the puff was estimated from the gaseous components in the mainstream smoke. The amount of oxygen consumed by smoking decreased with increasing alkali metals (Table 2). Thus, it can be considered that alkali metals inhibited the combustion of tobacco.

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A METHOD FOR THE SEMI-QUANTITATIVE DETERMINATION OF RESIDUES OF DISULFOTON, PHORATE AND TERBUFOS IN TOBACCO

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SUMMARY

An oxidative conversion of all residues of disulfoton, phorate or terbufos to the corresponding oxon sulfones (as confirmed by mass spectrometry) was performed on an aliquot of extract of dry tobacco. Thin-layer chromatography and Ackermann's esterase inhibition technique were employed for the separation and the semi-quantitative evaluation of the residues. High recoveries for the three above-mentioned insecticides (except terbufos) and their the most important metabolites (sulfoxides and sulfones) from dry tobacco were attained. The limit of detection of total residues was 0,1 mg/kg (expressed as active ingredient in dry tobacco).

INTRODUCTION

Disulfoton, phorate and terbufos are chemically related, very active, systemic organophosphorus insecticides. The first two are known and used for many years, so many papers were published about their metabolism in plants and also methods for determination of their residues (1-8). Terbofus came in use after 1970, but a lot of results obtained for the first two insecticides seem to be directly usable for it (9). The basic principle in the analysis of residues of disulfoton, phorate and terbufos in plants is that not the active ingredients themselves

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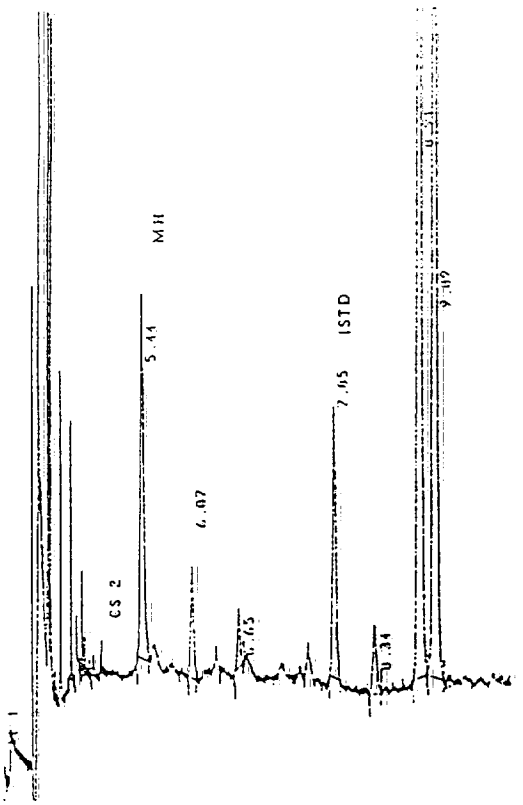
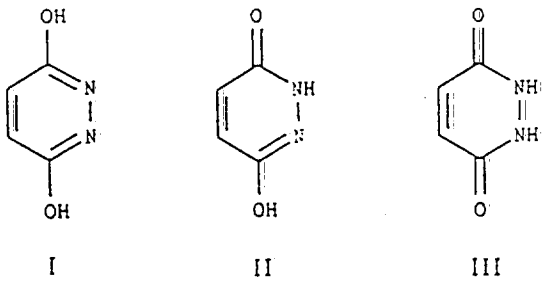
RESULTS AND DISCUSSION

Due to its polarity, maleic hydrazide cannot be extracted from the aqueous hydrolysis solution with an organic solvent. The derivative obtained by reaction with dimethyl sulfate is highly soluble in $CHCl_3$ and therefore can be easily extracted and analysed by gas chromatography (Fig. 1).





I II III

Maleic hydrazide could exist in any of the 3 tautomeric forms I-III (Fig. 2).

Katritzky and al [6] demonstrated that II is clearly predominent. This structure shows the presence of one hydroxy and one secondary amine group which are suitable for methylation. The methylation of MH with dimethyl sulfate results in the quantitative formation of the N-O-dimethyl derivative corresponding to isomer II. The positive proof of the identity of the derivative was obtained by GC-MS and 1H-NMR. In the mass spectrum, the molecular ion at m/z 140 corresponding to the N,O-dimethyl

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Sample preparation

Filler and tobacco leaves : 5 g of filler or ground tobacco leaves are introduced into a 250-ml flask and extracted with 100 ml of extracting solution for 2 h under reflux. After cooling, the extract is filtered through a folded filter, a 1-ml aliquot is taken for derivatization and introduced into a 5-ml reaction vessel.

Standard : 1 ml of calibration solution is introduced into a 5-ml reaction vessel and processed in parallel with the tobacco extracts.

Standard for GC-MS and 1H-NMR analyses : 1 ml of a 10-mg/ml solution of maleic hydrazide in 2 N HCl is introduced into a 5-ml reaction vessel. Derivatization is performed with 1 ml of dimethyl sulfate according to the procedure described below.

Derivatization and extraction

After neutralizing the extracting solution with NaOH 10 N and bringing its pH up to 11 with K2CO3 sat., 0.2 ml of dimethyl sulfate are added. The solution is shaken vigorously and let react at 75°C for 1 h. After cooling, 500 ul of chloroform are added, the flask is shaken vigorously by hand for 3 min and finally centrifuged (1 min at 3000 rpm). The organic layer is introduced into a 200-ul GC vial. 1 ul of the chloroform solution is injected into the GC.

Gas chromatography

GC conditions were as follows : split injector (1:30), 250°C; NP detector, 270°C; temperature program : 140°C, 3 min/ 5°C/min / 200°C / 20°C/min / 250°C, 16 min.

3 calibration replicates are first injected. The quantitation of samples is then performed using the internal standard method. MH residues are expressed as mg/g (dry weight tobacco basis).

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In 1980 acetate filter tips ruled the market by 48,7 %; the demand for cigarettes without filters and with paper filter tips only decreased. The rate of cigarettes with multi-filter tips containing activated carbon was already 16,3 % at this time. In 1989 the rate of cigarettes with multi-filter tips reached 81,4 %, and the rate of those containing also activated carbon, or other additives, was 46,7 %. Research and development of new brands and new production techniques were very active - according to demands - in the field of developing combined filters and filters containing various additives.

These various additives were primarily used to selectively filtering individual components of the mainstream smoke.

Besides the production of filters the range of the milder products was widened by the Hungarian Tobacco Industry from the end of the 1970's by brands which have been made with porous cigarette paper, taking advantage of the paper's improved burning characteristics. The first cigarette with reduced nicotine content appeared in the 1970's, also serving to meet the demands of a certain market segment. This kind of development was considerably promoted by work done in the Tobacco Research Institute to reduce the nicotine content in tobacco. As a result of this the range of products with less than 1 mg nicotine content per cigarette has considerably widened since then.

The use of air for the dilution of smoke has brought a great change in the development of low-tar cigarettes. The first brand with ventilated filter, the "Blue Symphony", was introduced on the market in 1982.

The use of filter ventilation enabled - besides the further reduction of the tar and nicotine content - the reduction of gaseous smoke components, primarily carbon monoxide.

The degree of filter ventilation of presently produced cigarettes varies between 20 to 50 %.

Besides the development of new brands - which employs agricultural and industrial research results in a more and more purposeful way -

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TLC determination

Method : Ascending, one dimensional developing in previously saturated tank. Layer : silica gel 60 G, self spreaded on 20 X 20 cm glass plate, layer thickness : 250 um immediately after spreading, used without activation, only dried over the night. Spotting : usually 25 ul extract is spotted on a plate 1,5 cm from the bottom. Four standards are always running on the same plate, dissolved in the same solvent as the sample and spotted in the same manner (five drops à 5 ul). Developing solvent : benzene-acetone 7 + 3. Height of developments : 15 cm. Time of development : about 35 minutes. Detection : dried developed plate is sprayed with enzyme solution until it is evenly wetted. Bromination is not used. The plate is incubated for 30 minutes in a chamber saturated with water vapour at 37°C. Still warm and wet, the plate is sprayed with freshly prepared solutions of 2-naphtylacetate and Fast blue salt B mixed in proportion 1:4 until the white spots on a violet background begin to appear (5 ml is enough for 1 plate).

RESULTS AND DISCUSSION

Approximate R_f values for oxon sulfones for described conditions are : 0,54 for disulfotonoxon sulfon, 0,62 for phorateoxon sulfone and 0,68 for terbufosoxon sulfone.

Two facts were basic in the developing of this relatively simple method of detection of disulfoton, phorate or terbufos toxic residues in tobacco :

1. Good selectivities and recoveries in described oxidation conditions with reference substances to the corresponding oxon sulfones.
2. Great sensitivity of Ackerman's esterase inhibition technique for the oxon sulfones.

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obtenus selon la nouvelle procédure sont en accord avec les résultats trouvés par la méthode colorimétrique (ISO).

INTRODUCTION

Maleic hydrazide (3.6-dioxo-1.2-dihydro pyridazine) (MH) is a systemic plant growth-regulator which is used extensively for tobacco-sucker control. MH is usually applied to the upper half or third of the tobacco plant within 24 h after topping. It is subsequently found throughout the plant due to absorption and translocation. MH inhibits cell division without affecting cell elongation, thus preventing the growth of newly developing suckers without retarding the growth of more mature leaves. A β-D-glucoside, representing 15 % of the free MH fraction, was identified in tobacco, wheat and apple [1]. Results from relevant literature [2] show that average MH residues on US flue-cured tobaccos have remained constantly above 100 ppm since about 1974, and individual values on raw-leaf tobacco up to 300 ppm were measured. Average values obtained in our laboratories on the latest crops, i.e., 1985 to 1989, confirm the published values. As a consequence, residues found on American cigarettes are significant. For example, an increase from 39 ppm in 1973 to 66 ppm in 1984 was observed [2].
Despite the fact that no evidence of harmful effects was obtained [2], a maximum amount of 80 ppm has been recommended in Germany which requires an analytical procedure for MH determination on tobacco.
This determination is now being performed by a colorimetric procedure which was adopted as an ISO Standard Method [3] and an official method of the Association of Official Analytical Chemists [4]. The procedure consists in a hydrolytic reduction of MH to hydrazine by zinc in an aqueous sodium hydroxide solution. The hydrazine is subsequently steam distilled and collected in an acidic solution of p-dimethyl-aminobenzaldehyde to form a yellow compound with an absorption maximum at 455 nm.

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but their oxidative metabolites (sulfoxides and sulfones as the main, oxon sulfoxides and oxon sulfones as the minor residues) are to be looked for and determined. Because of such a great number of possible compounds, the residue analysis becomes difficult. The TLC method developed represents an approach in the residue analysis of disulfoton, phorate and terbufos in tobacco, usable for screening or confirmation purposes.

EXPERIMENTAL

Reagents

(a) Solvents : acetone, benzene, n-hexane, dichloromethane, ethanol - all p.a. (Merck).

(b) Celite 545.

(c) Oxidation reagent : 6,4 g $KMnO_4$, 50 ml acetic acid and water to 1000 ml.

(d) Na_2SO_3, saturated solution in water.

(e) Na_2SO_4 anhydrous.

(f) Silica gel 60 G (Merck 7731).

(g) Beef liver water extract as source of esterase, diluted as necessary for optimal working conditions.

(h) 2-naphtyl acetate, 1,25 mg/ml ethanol, freshly prepared.

(i) Fast blue salt B, 1,25 mg/ml water, prepared before spraying.

(j) Reference substances : phorate (98% pure), terbufos, terbufos sulfoxide, terbufos sulfone, terbufosoxon sulfoxide and terbufosoxon sulfone (all at least 90% pure) kindly supplied by Cyanamide of Great Britain Ltd. (Gosport, Hampshire), disulfoton (95% pure) Sandoz, disulfoton and phorate sulfoxides prepared from technical insecticides (active ingredient (a.i.) in Solvirex 10 and Thimet G 5) by selective oxidation with H_2O_2, disulfoton and phorate sulfones, prepared from technical a.i. by selective oxidation with neutral aqueous solution of $KMnO_4$, disulfotonoxon sulfone, phorateoxon sulfone, prepared from technical a.i. by selective oxidation with weakly acidic

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The oxidation step in the procedure has also a considerable cleaning effect on sample, which enables application of an aliquot of the sample for TLC as big as to reach the desired limit of detection. The work is somewhat easier with terbufos and phorate residues because of low detection limits of their oxon sulfone (about 0.1 ng) comparing with the detection limit of disulfotonoxon sulfone (about 2 ng). There are more variants of TLC application of esterase inhibition technique (14-18). It is well known that the sensitivity depends on the source of enzyme and its concentration, but it seems that the way of visualisation is also important. Published detecting limits of disulfotonoxon sulfon and phorateoxon sulfone by Mendoza's esterase inhibition technique (in something different TLC conditions) are much higher (400 ng and 5 ng) (19). The basic relationship that the detection limit for disulfotonoxon sulfon is considerably higher than for the other two compounds is , however, confirmed.

The recovery experiments in presence of tobacco with three insecticides and their three oxidation products at the residue levels (0,5 mg/kg to 1 mg/kg) were satisfactory except for terbufos (only about 20% recovery). It seems that the sample consumes too much oxidant, so perhaps a greater concentration of $KMnO_4$ is needed. However, this fact does not create such a problem if one keeps in mind that terbufos itself is not expected to be present as residue in dry tobacco.

Because of the extremely great sensitivity of enzymatic detection all usually precautious as for trace analysis are necessary - careful cleaning of glassware, running of "reagent blind". Running of untreated tobacco samples is also recommended. Although the method developed here does not need much work and chemicals it is perhaps possible to perform micro analysis on a smaller aliquot of tobacco extract (practical for multi-residual and confirmating analysis), which remains to be studied.

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ACKNOWLEDGMENT

Special thanks goes to B. Kralj from "Institute J. Stefan" in Ljubljana for the mass spectra.

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In order to check the range of linearity of the detector response a linear calibration graph was obtained for each of the four carbohydrates by plotting peak areas vs. concentrations with correlation coefficients in the range 0.99939-0.99996.

TABLE 3
RANGE OF CONCENTRATIONS OF SOME SUGARS IN TOBACCO CULTIVARS

Cultivars	Inositol (%)	Glucose (%)	Fructose (%)	Sucrose (%)
Oriental	0.69÷1.70	2.0÷ 9.5	2.4÷ 8.5	traces
Bright	0.72÷1.60	3.2÷17.0	4.9÷12.2	0.5÷6.0
Kentucky	1.20÷1.40	0.5÷ 3.0	1.3÷ 2.5	traces

The linearity of the responses was confirmed using the rhamnose as internal standard. Linear calibration graphs were obtained by plotting the ratio A_c/A_r vs. concentrations, were A_c is the peak area of each carbohydrate and A_r is the peak area of rhamnose. The correlation coefficients were in the range 0.99984-0.99999. Through the described procedures anion exchange liquid chromatography and pulsed amperometric detection proved to be efficient instruments for the separation, the identification and the quantitative determination of low-molecular weight carbohydrates in tobacco leaves and in cigarette filler.
Other aspects of our study, such as the identification of some unknown peaks present in the report chromatograms and the quantitative determination of other carbohydrates, present in lower concentrations, are currently being studied.

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Fig. 1 Mass spectrum of phorateoxon sulfone

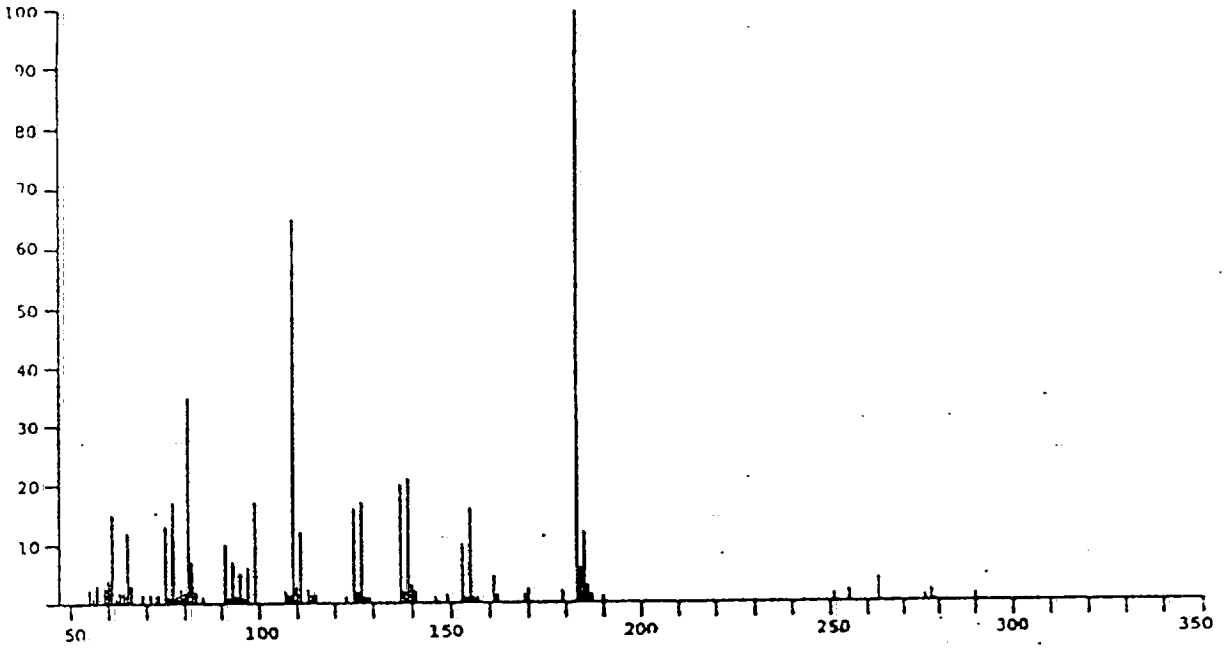
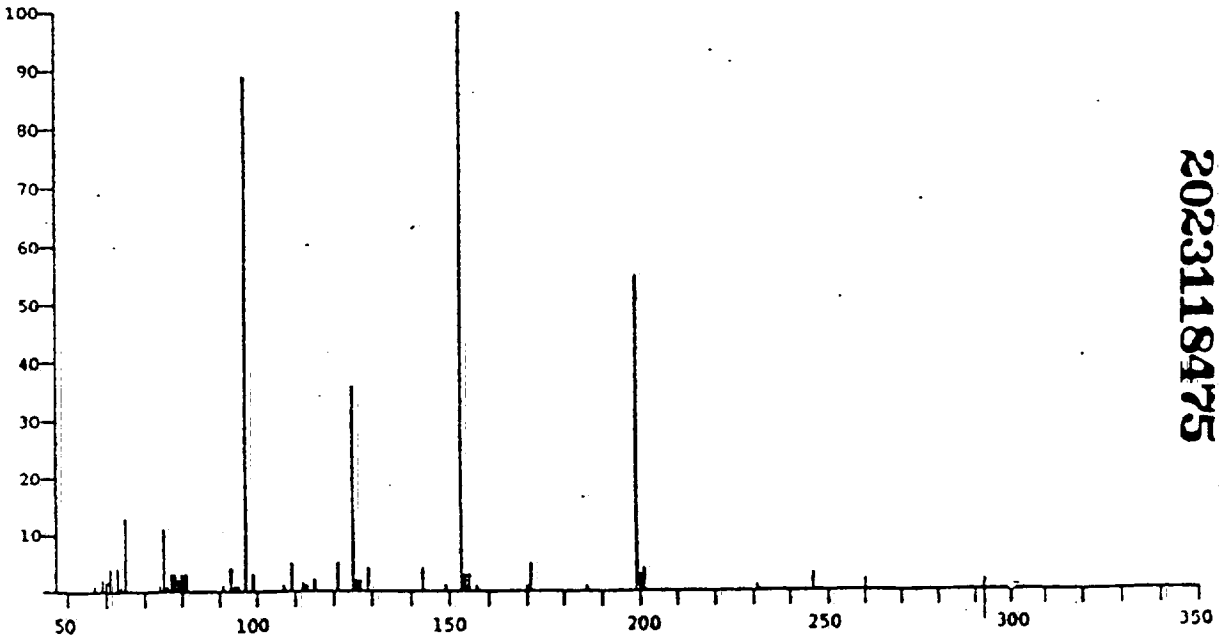


Fig. 2 Mass spectrum of phorate sulfoxide



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The other two acid, 2-methyl-and 2-ethyl-5oxohexanoic acid, having the similar skeleton with 2-isopropyl-5-oxohexanoic acid, can also be synthesised with the same method and the yield is 30~45%. And these two acids and their methyl and ethyl esters have not been reported to exist in tobacco.

2. The odor of synthesised compounds and their effect on cigarette smoke are given below.

TABLE

ODOR AND SMOKE FLAVOR OF THE SYNTHESISED COMPOUNDS

Compound	Odor	Smoke Flavor
2-Isopropyl-5-oxohexanoic acid	Hay-like, Fruity, Sour-sweet	Oriental character, Sweet, Mellowing, Slightly Grassy, Smoothing
2-Ethyl-5-oxohexanoic acid	Cream, Sour-sweet	Hay-like, Bitter
2-Methyl-5-oxohexanoic acid	Melon-like, Sweet, Green	Roasted, Flue-cured chracter, Green
Ethyl 2-isopropyl-5-oxohexanoate	Musty, Winey	Smoothing, Adds body, Sour, Sweet
Methyl 2-isopropyl-5-oxohexanoate	Fruity, Musty	Woody, Hay-like, Green, Smoothing
Ethyl 2-ethyl-5-oxohexanoate	Pearlike、Sweet	Sweet、Roasted
Methyl 2-ethyl-5-oxohexanoate	Musty-cereal	Green、Burnt-woody
Ethyl 2-methyl-5-oxohexanoate	Roasted, Green	Sweet, Smoothing, Flue-cured character, Roasted
Methyl 2-methyl-5-oxohexanoate	Almond、Bean	Flue-cured character, Roasted Smoothing, Hay-like

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2980,2957,2882, 1737,1720,1464,1437,1365,1265,1206,1164,1128,1018,985,842; MS:158(MW),127,126,115,101,99,71,59,43).

Ethyl 2-methyl-5-oxohexanoate was collected at 82-84℃/4mmHg (IR:2961,2920, 1723,1712,1463,1446,1370,1250,1161,1022,858; MS:172(MW),127,126,115,101, 99, 73,45, 43).

Methyl 2-ethyl-5-oxohexanoate was collected at 80-81℃/3mmHg (IR: 2945,2860, 1725,1710,1606,1468,1413,1382,1350,1143,1071,984,850,797; MS:172(MW),141,140, 115,113,112,71,59,43).

Eehyl 2-ethyl-5-oxohexanoate was collected at 94-96℃/4mmHg (IR:2957, 2852, 1724,1707,1477, 1440,1384,1348,1149,1020,942,857; MS:186(MW), 143, 141, 140, 129,115,112,73,71,57,43).

Methyl 2-isopropyl-5-oxohexanoate was collected at 96-99℃/3mmHg (IR: 2963, 2886,1730, 1713,1462,1433,1370,1251,1198,1157,1047,852; MS:186(MW),155,154, 143,127,115,111,71,57,43).

Ethyl 2-isopropyl-5-oxohexanoate was collected at 103-105℃/3mmHg (IR:2964, 2938,1728,1467,1372,1177,1156,1027,855; MS:200(MW),157,155,154,143,127,112, 111,71,55,43).

Note: IR spectra were determined with a PE-580B IR spectrometer. MS spectra were carried out on a HP-5988 MS spectrometer.

SENSORY TEST All of the prepared acids and esters were injected to blended type and flue-cured type cigarettes at 0.01% of the tobacco weight. The effect of these compounds on cigarette smoke were evaluated by smoking panel.

RESULTS AND DISCUSSION

1. 2-Isopropyl-5-oxohexanoic acid can be synthesised in one-step with the yield of 45.3%. Since the synthesis was completed without the seperation of condensation product, ethyl ethoxycarbonyl-2-isopropyl-5-oxohexanoate, this method is relatively more covenient and applicable than other methods previously reported.

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INTRODUCTION

99 % of tobacco consumption in Hungary consists of different cigarette brands.

Taking the average daily cigarette consumption into consideration, the number of smokers in Hungary is approximately 4 million, which is almost 40 % of the total population. Smoking is especially wide-spread among the working population which shows how much the population as a whole is concerned. According to our experiences and to consumption data the propaganda against smoking has not shown a considerable effect so far. Cigarette consumption in Hungary has been between 25.6 to 26.9 billion pieces per year during the last ten years. A reasonable alternative to the attempt of changing the smoking habits would be to lower the amount of smoke constituents of the different cigarette brands.

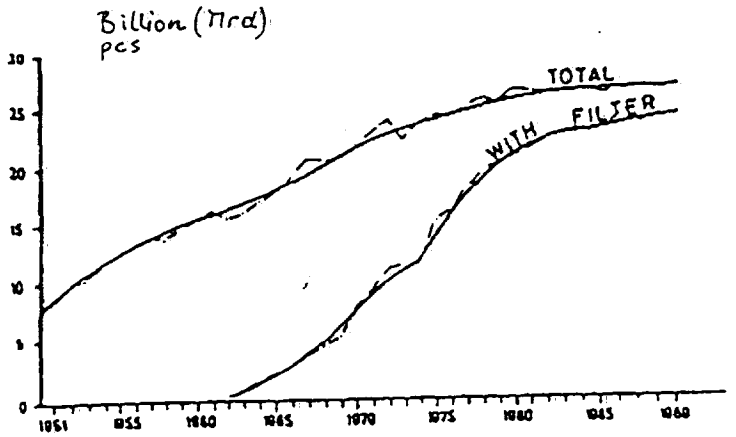
RESULTS AND DISCUSSION

The first figure illustrates cigarette consumption from 1950 until today and the change of the rate of filter tipped cigarettes within the total consumption.

Fig. 1

TRENDS OF CIGARETTE CONSUMPTION IN HUNGARY

PERIOD 1950 - 1989



The first section of the line, illustrating the total consumption, grew in a linear way until the end of the 1970's when the rate of growth began to decrease and, practically, this has not changed

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In searching optimum oxidation, many oxidants and conditions were tested. Until now in the most cases for the same purpose used reagent, 3-chloroperbenzoic acid (K&K Laboratories!) (6,11) was compared with proposed $KMnO_4$ in weak acid conditions. The oxidation products were analysed by TLC with $PdCl_2/J_2$ detection (12). In all cases of oxidation of microquantities of named insecticides and their oxidation products the $KMnO_4$/ acetic acid reagent was superior. The oxon sulfones were the only products with good recoveries. Also, the oxon sulfones were stable in the oxidation conditions. Increased concentrations of acetic acid in oxidation solution resulted in worse recovery of oxon sulfones - a result which has been known long ago for the oxidation of phorate (11). With neutral solution of $KMnO_4$ (0,1 or 0,5 N) the P=S compounds give sulfones (and oxon sulfones in traces) and only P=O compounds oxon sulfones as oxidation products. This reaction is usually used in the methods for the GLC determination of total residues of this group of insecticides (1,3,7). Although the $PdCl_2/J_2$ detection makes possible to differentiate between sulfoxides and oxon sulfones in doubtful TLC separation (because of different colours of the spots), the MS identification of oxon sulfones was also performed, (9,13,14). The molecular masses of corresponding sulfoxides and oxon sulfones are equal and the molecular peaks in our conditions of taking off the mass spectra of low resolution (mass spectrometer CEC 21-110 B, ionisation energy : 70 eV, source temperature : 60-100°C, direct insertion of compounds) were weak for both types of compounds, but the differences in MS are obvious and well usable for the identification : the most intensive and at the same time characteristic peaks arise from fragments after delta cleavage of the disulfoton derivate with regard to phosphorous atom and further elimination of two ethen molecules (m/e 197, 169 and 141 in MS of disulfotonoxon sulfon). This corresponds to gamma cleavage in phorate and terbufos oxon sulfones (m/e 193, 155 and 127). Peaks in common for all three MS, give alpha cleavage (m/e 137, 109 and 81) Characteristical for the MS of all terbufos derivatives is the peak at m/e 57 (t-Bu, usually the base peak), which is the main difference to the MS of phorate derivatives.

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CORESTA

THE EVOLUTION OF THE SMOKE YIELD OF HUNGARIAN CIGARETTES

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SUMMARY

The objective of this study was to examine the technological brand development and other factors which account for the decreases that have occurred in the tar, nicotine and CO deliveries from Hungarian cigarettes. Cigarette consumption trends dating back to 1950 will be presented. Statistical evaluation of mainstream smoke deliveries during 1985 to 1990 will be made.

Cigarette consumption in Hungary increased almost linearly with time from 1950 to 1980. Increasing attention has been given to the deliveries and composition of smoke.

Production of filter cigarettes started in 1962 and produced the first significant change in mainstream composition of Hungarian cigarettes. From that date market proportion of filter cigarettes has increased annually and exceeded 90 % in 1989.

In the 1970's brands appeared with multi-section filters containing active carbon, and later on various additives. Currently the larger part of the dominating brands are multifilter cigarettes. This paper gives a brief review of filter development, introduction of filter ventilation and results from the latest brand development. It also indicates those directions of cigarette production development by which smoke tar content was reduced.

The analysis shows that tar content of mainstream smoke was reduced by about 20 % compared to 1985. A smaller reduction was experienced in nicotine content, while the CO content did not change substantially.

Further decreases in smoke composition could be achieved by spreading of new brands. Introduction of these on the market is hindered, partly by the extremely strict advertisement restriction and partly by the unfavourable prices.

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believe that alkali metals are not directly related with the carbonaceous reduction of CO_2 in cigarettes.

EXPERIMENTAL

Unblended non-filter cigarettes were made from the cutter of Bright tobacco cultivars. The width of the cut shreds was 0.8 mm. Aqueous solutions of potassium malate and sodium malate were sprayed onto the shreds. The potassium and sodium contents added to the shreds was measured using Zeeman effect atomic absorption spectro-photometer (HITACHI type 6100). The length and circumference of the cigarettes were 70 mm and 25 mm, respectively. Cigarette paper with a permeability of 10 ml/cm^2/min/100 mmw.g. was used. After conditioning at 22°C, 60% R.H., each sample was selected by weight to keep the fractional volume of the cigarettes constant (0.31 or 0.32). Cigarettes were smoked on a smoking machine under standard smoking conditions. The concentration of CO in the mainstream smoke was measured by a non-dispersive infra-red analyzer, and the concentration of O_2 was measured by an oxygen meter (IIJIMA Type RO-101).

Thermogravimetry was carried out using a TGS-1 Thermo-balance (Perkin-Elmer). Powdered tobacco with and without the additives was heated at a rate of 20°C/min under a flow of air or nitrogen (200 ml/min). The additives were potassium malate and sodium malate. In order to investigate the effect of alkali metals on the oxidation of tobacco char, tobacco chars were prepared by the method described by Muramatsu *et al.* (5). Tobacco shreds were heated in an electric furnace to 550°C at a constant heating rate of 20°C/min and then maintained at this temperature for 2 hours under a flow of nitrogen. DSC measurements of the following 2 samples were carried out in air atmosphere using DSC-41M (Shimadzu).

Sample A: Mixture of untreated tobacco char and K_2CO_3
Sample B: Char made from tobacco treated with potassium malate

The surface area of chars of Sample B was measured with the BET gas adsorption technique using nitrogen as the adsorbate gas. The equipment used was a Belsorp 28 (NIHON BELL). Before the measurement, sample chars were dried for 16 hours at 150°C under vacuum.

Ash samples were obtained from cigarettes which had been smoked under standard smoking conditions. Char samples of the burning cone were obtained from cigarettes which had been extinguished by liquid nitrogen after 9 puffs. Both samples were powdered in mortars. The amount of carbon in the samples was determined by a CHN recorder (Yanaco MT-2type).

The maximum temperature of the solid phase at the surface of the burning zone during a puff was measured with a scanning infra-red camera interfaced to a digital image processor (Fujitsu INFRA-EYE 5000).

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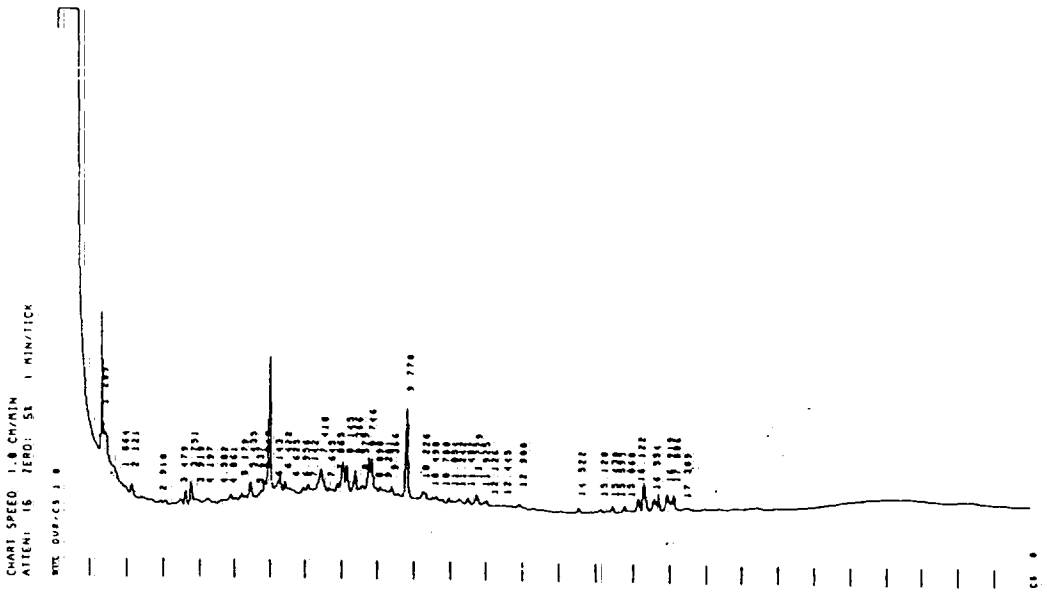

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CHANNEL: 1B - 1 TITLE: 12:32 14 APR 87

SAMPLE: 3 - N METHOD: RF1B CALCULATION: AI - ANALYS

PEAK NO	PEAK NAME	RESULT AREA%	TIME (MIN)	TIME OFFSET	AREA COUNTS	SEP CODE		WI/2 (SEC)
1		7.2188	1.209		105872	BV		1.00
2		1.0249	1.375		15031	VV	?	1.50
3		1.7200	1.406		25238	VV		1.19
4		1.1264	1.441		16520	VB	?	1.13
5		0.9124	2.121		13382	BB		3.38
6		0.6835	3.479		10025	BB	?	4.94
7		1.1379	3.610		16689	BV		3.00
8		1.0397	3.751		26381	VV		3.13
9		1.2819	4.861		18800	VV	?	7.06
10		0.9809	5.179		14386	VV	?	6.31
11		2.2299	5.435		32704	VV	?	6.88
12		0.7772	5.708		11399	VV	?	4.31
13		2.0598	5.843		30210	VV	?	4.50
14		12.9972	5.958		190619	VV		3.06
15		1.4005	6.203		20540	VV	?	3.94
16		2.0577	6.277		30179	VV	?	8.00
17		1.4581	6.422		21971	VV	?	4.50
18		0.7018	6.956		10292	BV	?	4.44
19		0.8996	7.064		13194	VV		4.00
20		5.2384	7.418		76810	VV	?	7.38
21		0.7893	7.645		11576	VV	?	3.06
22		1.2154	7.865		17825	VV		4.25
23		5.0737	8.021		74412	VV	?	7.69
24		3.1206	8.145		45885	VV		3.69
25		2.9149	8.366		42751	VV		3.44
26		1.4832	8.579		21753	VV	?	4.38
27		4.0578	8.746		59513	VV		4.13
28		3.5503	8.826		52069	VV	?	3.75
29		0.9951	8.898		14595	VV	?	10.69
30		1.1329	9.050		16615	VV		3.94
31		0.6397	9.133		10262	VV	?	2.31
32		1.2852	9.366		18849	VV		3.31
33		7.7919	9.770		114277	VV		3.38
34		0.7885	10.226		11565	BV	?	4.00
35		1.3013	11.242		19085	VV		8.00
36		0.8678	11.482		12727	VV		4.38
37		1.7755	11.729		26048	VV		5.00
38		0.6921	15.742		10150	VV		4.19
39		1.5566	16.122		22829	VV		4.94
40		3.4694	16.286		50883	VV		4.63
41		1.6228	16.554		23801	VV		6.63
42		1.7790	16.680		26091	VV		4.50
43		2.1953	16.919		32196	VV		6.38
44		2.0542	17.006		30127	VV		6.06

TOTALS: 100.0000 1466618

DETECTED PKS: 96 REJECTED PKS: 52

MULTIPLIER: 1.00000

NOISE: 34.3 OFFSET:133864

ERRORS:
AOC OVERANGE

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CUT TOBACCO STORAGE

Hinrich Elmenhorst, M. Brinkmann AG, Bremen, Germany

Abstract

The effect of the storage time of cut tobacco on tobacco and smoke chemistry, physical cigarette parameters, and sensory properties has been studied in six commercial blends. all available evidence suggests that the storage of cut tobacco for up to 26 weeks at 21°C and 70% RH has no detrimental effect on aroma and taste and hence on the acceptability of the product.

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This was preceded by a significant improvement of the processing lines.

The modernization of sanitary research, tobacco processing and cigarette production increased the demand for buying more appliances and improving the ones we have, in the field of development on the one hand, and in the field of quality control, on the other.

Since 1985, there has been a regular control of smoke delivery covering all brands produced by the industry. The tar, nicotine and carbon monoxide content in the mainstream smoke of cigarettes produced in Hungary has changed as shown by table one.

TABLE 1

AVERAGE TAR NICOTINE AND CO CONTENT OF HUNGARIAN CIGARETTES

	1985.	1986.	1987.	1988.	1989.
TAR mg/cig.	23,29	22,10	21,0	20,3	18,7
NICOTINE mg/cig.	1,17	1,10	1,09	1,12	1,05
CO mg/cig.	19,40	20,2	20,4	19,8	19,1

Compared to 1985, as a result of development :

- the tar content has decreased strongly, with about 20 %; the 5 to 10 % decrease in the nicotine content is not a strong as this, but it is still a favourable tendency;

- the constancy of the carbon monoxide content can be put down to the fact that, although, the number of brands with ventilated filter grew from 7 to 12 between 1985 and 1989, their rate on the market during the sme time grew only from 5,6 % to 6,3 %.

The results in the development of new brands can be well illustrated by the characteristics of the mainstream smoke of the two most popular cigarette families, the "Sopianae" and the

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lower significance than the condensate ones. Under low oxygen atmosphere conditions, we could expect an increase in CO and a decrease in CO2 by volume yields (5). That was observed, but the values expressed by weight - after taking account of barometric pressure and puff count - remain practically unchanged, suggesting a no so different burning conditions to explain the differences in sidestream condensate yields. All these considerations support the suspicion of an artifact of the sidestream collection method used, involving the filter efficiency in particular.

The sidestream condensate yield variations observed for different barometric pressures could be genuine, but the results of puff-count and sidestream CO and CO2 make one think that some details of the method could be masking other factors affecting this experiment. Further investigation is necessary to demostrate if the sidestream Cambridge filters are equally efficient at collecting condensate at different barometric pressures.

CONCLUSIONS

1 Earlier results regarding the influence of barometric pressure on cigarette smoking are confirmed: the lower the barometric pressure the higher the puff-count, but no important differences are to be found in mainstream yields.

2 Gas-phase CO and CO2 yields are not significantly affected by barometric pressure, either main- or sidestream.

3 An increase of 7 % in sidestream condensate yields is obtained when barometric pressure is 8.6 % lower.

4 Increasing the chimney flow rate is a practical way to compensate for the effect of low barometric pressure on sidestream condensate yields.

5 Further investigation would be necessary to clarify if the observed effect is genuine or a consenquence of a loss of efficiency in Cambridge filters when the barometric pressure increases.

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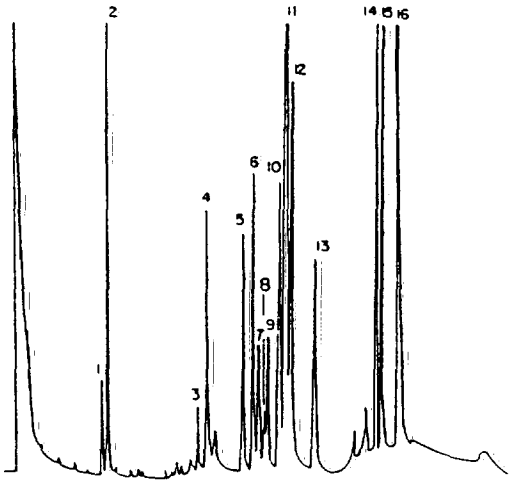

Fig. 1 - GASCHROMATOGRAM OF A STANDARD MIXTURE OF SYNTHETIC PYRETHROIDS OBTAINED BY USING SPLIT-SPLITLESS INJECTION PORT. THE NUMBERS OF THE PEAKS CORRESPOND TO THE COMPOUNDS REPORTED IN TABLE 2.

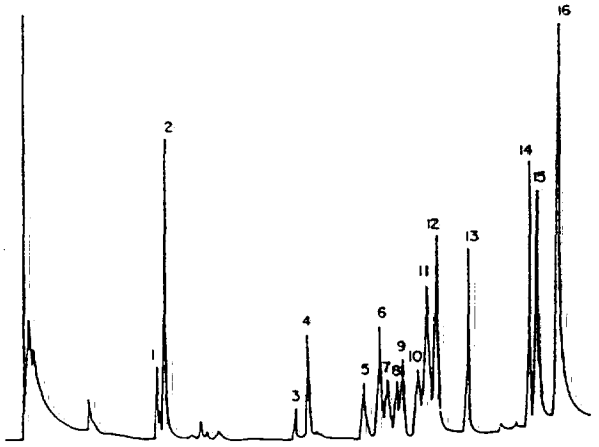

Fig. 2 - GASCHROMATOGRAM OF A STANDARD MIXTURE OF SYNTHETIC PYRETHROIDS OBTAINED BY USING COLD SPLIT-SPLITLESS INJECTION PORT. THE NUMBERS OF THE PEAKS CORRESPOND TO THE COMPOUNDS REPORTED IN TABLE 2.

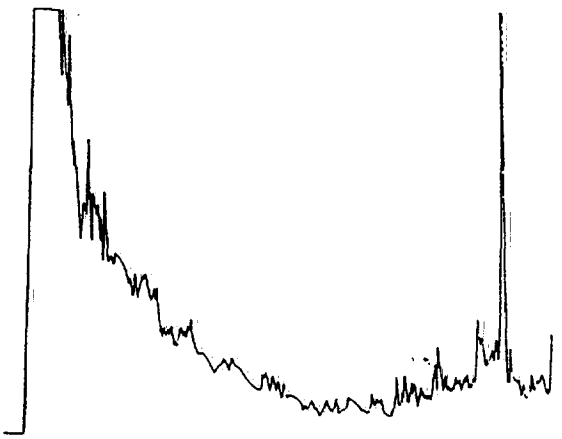

Fig. 3 - GASCHROMATOGRAM OF UNTREATED TOBACCO

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DISCUSSION

The DSC curve of tobacco char in air is made up of 2 peaks. Muramatsu *et al.* considered that the first peak of DSC curve is attributable to oxidation of a more reactive portion of the char (5). In the case of cellulosic char with sodium, it is reported that the first peak corresponds to the oxidation of the aliphatic component and the second peak corresponds to the oxidation of the more stable aromatic component.(6). As shown in Figs. 4 and 5 the first peak of the DSC curve disappeared and the surface area decreased in the case of carbonaceous residue of tobacco treated with alkali metal salts. It is obvious that alkali metal salts form a more stable char in the decomposition process of tobacco.

Actually, as shown in Table 2, the amount of oxygen consumed during the puffs decreased, although the yield of the char from the burning cone was independent of the amount of additive alkali metals. Also, the carbon content in the ash, which fell naturally during smoking, increased with increasing amount of alkali metal salts. These results of the measurements of cigarettes corresponded with those of pyrolysis. The more stable char reduces the heat release on combustion. Actually, the temperature of the burning cone was lowered by the addition of alkali metals.

Consequently, alkali metals form a stable char in the decomposition process of tobacco, so that the formation of CO in the combustion decreases. Further, since the more stable char reduces the heat release, the temperature of the burning cone falls, and the formation of CO through carbonaceous reduction is reduced.

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DETERMINATION OF FREE AND GLYCOSIDICALLY BOUND MALEIC HYDRAZIDE IN TOBACCO

DETERMINATION DE L'HYDRAZIDE MALEIQUE LIBRE ET SOUS FORME DE GLYCOSIDE DANS LE TABAC

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Neuchatel, Switzerland

SUMMARY

Maleic hydrazide (MH), a systemic plant-growth regulator is used extensively for tobacco-sucker control. Due to the high residue levels found on raw-leaf tobacco, the development of a fast, specific and simple procedure is of interest for the determination of MH on tobacco. A new method was established involving the methylation of MH with dimethyl sulfate and the gas chromatographic quantitation of the derivative using a specific nitrogen-phosphorous detector. Results obtained by the GC procedure are in accordance with the values obtained by the colorimetric (ISO) procedure.

RESUME

L'hydrazide maléique (HM) est un régulateur systèmique de croissance qui est utilisé extensivement pour le traitement inhibiteur des bourgeons du tabac. Etant donné les valeurs élevées des résidus détectés sur les feuilles de tabac, le dévelopement d'une méthode rapide, spécifique et simple rencontre un grand intérêt. Une nouvelle procédure a été mise au point qui inclut la méthylation de HM avec le diméthyl sulfate, suivie de la quantification du dérivé par chromatographie gazeuse en utilisant un détecteur spécifique azote-phosphore. Les résultats

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2-Isopropyl-5-oxohexanoic acid has hay-like, fruity and sour-sweet odor and can give the slightly grassy smell and Oriental tobacco character in cigarette smoke. As the isopropyl radical in C-2 is substituted by methyl to form 2-methyl-5-oxohexanoic acid, the melon-like, green odour and a fruity, roasted flavour on smoke are obtained.

The esters of 2-methyl and 2-isopropyl-5-oxohexanoic acid have similar behavior in cigarete smoke. They enhance and improve the flavor of smoke and reduce the irritation of blended type cigarette as well as flue-cured type cigarette

The effect of 2-ethyl-5-oxohexanoic acid and its methyl and ethyl esters on smoke is not significant.

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"Symphonia" as well as that of the latest type of the first Hungarian low nicotine cigarette brand, called "Helikon".

The "Sopianae" products' share on the market was 42,9 % while that of the "Symphonia" products was 35,8 %. In short, these brands ruled more than three-quarters of the Hungarian market in 1989.

As it can be seen from table 2 the most recent version, that is, "Sopianae Nivo", contains only half as much tar and nicotine as "Sopianae Multi-filter" brand.

TABLE 2

MAINSTREAM SMOKE COMPONENTS OF SOPIANAE CIGARETTE BRANDS IN 1989

BRAND	TAR mg/cig.	NICOTINE mg/cig.	CO mg/cig.
Sopianae Multifilter (80 mm)	18,2	0,99	19,8
Sopianae 100	13,3	0,81	17,1
Sopianae Nivó 100	9,5	0,59	15,5

As similar development can be observed in case of the other most popular product, "Symphonia" (table 3). With this cigarette family a significant reduction of the CO-content could also be achieved.

TABLE 3

MAINSTREAM SMOKE COMPONENTS OF SYMPHONIA CIGARETTE BRANDS IN 1989

BRAND	TAR mg/cig.	NICOTINE mg/cig.	CO mg/cig.
Symphonia red	19,4	1,16	20,2
Symphonia blue	16,1	1,10	16,2
Symphonia yellow	9,1	0,65	9,8

In the fourth table we find data about the smoke of "Helikon"

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TABLE 3

DETECTION AND DETERMINATION LIMITS FOR SYNTHETIC PYRETHROIDS

Pyrethroids	Detection limit (ppm)	Determination limit (ppm)
Alfamethrin	0.01	0.02
Cyfluthrin	0.02	0.05
Cypermethrin	0.01	0.02
Deltamethrin	0.01	0.02
Flucythrinate	0.02	0.05
Fluvalinate	0.01	0.02
Permethrin	0.01	0.02
Tetramethrin	0.01	0.02

TABLE 4

RECOVERY OF SYNTHETIC PYRETHROIDS FROM FORTIFIED TOBACCO

Pyrethroids	Recovery %
Alfamethrin	95
Cyfluthrin	97
Cypermethrin	95
Deltamethrin	110
Flucythrinate	108
Fluvalinate	104
Permethrin	95
Tetramethrin	90

Finally, as an example of routine determination, in figures 4-6 some chromatograms of field-treated tobacco samples are shown.

In conclusion, an effective procedure has been developed for the extraction of eight synthetic pyrethroids from tobacco and for a simple and rapid clean-up of these extracts in order to carry out the analysis of the pyrethroids at the residue level by GLC-ECD.

On the basis of structural similarities, one can assume that this method, which has been successfully used in our laboratory for routine determinations, can be extended for the residues analysis of other pyrethroid insecticides.

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derivative is very abundant (92 %) and its fragmentation gives main signals at m/z 112 (36%), 80 (47%) and 69 (100%) which is the base peak of the spectrum. The molecular ion loses a molecule of CO producing an ion at m/z 112 which loses formaldehyde, resulting in a peak at m/z 80. The base peak at m/z 69 results from the successive losses of CH_3, N_2 and CO from the molecular ion.

The 1H-NMR spectrum consists in the following 3 signals : δ =3.6 ppm, S, 3H, CH_3-N; δ= 3.8 ppm, S, 3H, CH_3-O; δ =6.9 ppm, S, 2H, H-C=C-H. The presence of 2 distinct signals at 3.6 and 3.8 ppm corroborates the information from the mass spectrum showing that the derivative obtained corresponds to tautomer II.

Barbital was chosen as internal standard because of the similarity of its structure with that of MH. This ensures that both compounds react and can be extracted similarly. The reaction of barbital with dimethyl sulfate produces the N,N-dimethyl derivative. This reaction was described by Martin [7] in 1966.

The NP-detector response is linear (r^2 = 0,999) within the whole range tested, i.e., from 10 to 600 ppm as shown in Fig.3.

Recoveries of MH from tobacco never treated with MH in the field when fortified with 80 ppm average 95 %. A relative standard deviation of 7 % was obtained at both 10 and 70 ppm on tobacco samples. The detection limit of the method determined on cigarette filler is 5 ppm. A comparative study between results obtained by the GC and colorimetric (ISO) procedure was performed. 65 samples including commercial cigarettes as well as tobacco leaves were analysed by both methods : ISO values reported as a function of the GC values (Fig.4) show a good agreement between both procedures. The slope of the correlation line is 0.972, the intercept +4.5 ppm and the correlation coefficient r^2 = 0.985. The 4.5 ppm intercept may result from the lower specificity of the ISO method.

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Supelclean disposable SPE tubes (LC-Florisil 6 ml, 1 g) filled with Florisil were used.
All the reagents were pesticide-grade.
Pyrethroids stock standard solutions (1000 µg/ml in hexane) are stable for at least 1 month if stored in the dark at 4 °C. Working standard solutions were prepared daily.
As internal standard mirex can be used at a concentration of 5 µg/ml.

-Procedure.
Weigh 2 grams of ground tobacco in a jar, add 100 ml of acetone:water 9:1 and extract for 5 hours using a mechanical stirrer. After filtration through filter paper Whatman N.3 or equivalent, transfer the solution into a separatory funnel and extract with 4 x 25 ml portions of hexane. Filter the combined portions of organic phase through anhydrous sodium sulphate and evaporate to about 1 ml with vacuum rotatory evaporator at 40 °C. Using a Pasteur pipette transfer the hexane extract onto a short column of anhydrous sodium sulphate on the top of a SPE tube previously conditioned with 2 ml of hexane. Elute with hexane (3 ml) followed by seven fractions (2 ml each) of a mixture hexane:diethylether 9:1 and then by diethylether (20 ml). Discard the first three fractions and collect the other ones. In table 1 the pyrethroids distribution in the fractions eluted from SPE tube is shown. Combine the collected fractions, concentrate the resulting solution to 2 ml by using a stream of clean, dry nitrogen and inject 1 µl into gas-chromatograph. It is possible, of course, to inject into gas-chromatograph 1 µl of each fraction eluted from SPE tube.

TABLE 1
SYNTHETIC PYRETHROIDS DISTRIBUTION IN SPE-FRACTIONS

Pyrethroids	SPE-Fractions					
	4	5	6	7	8	9
Permethrin	++	--	--	--	--	--
Cyfluthrin	++	++	++	--	--	--
Cypermethrin	++	++	++	--	--	--
Alfamethrin	++	++	++	--	--	--
Deltamethrin	--	--	++	++	--	--
Fluvalinate	--	--	++	++	--	--
Flucythrinate	--	--	--	++	++	--
Tetramethrin	--	--	--	--	--	++

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was performed. Then t-tests were applied to the different comparisons of results, Madrid versus Sevilla. A summary of mainstream results is presented in Table 3.

The results showed increasing values of puff-count for all the samples investigated when the altitude increased, but no effect on this parameter was observed when the flow rate increased up to 3.5 litre per minute. On average, there was found to be a 3 % difference in puff-count within the ISO accepted range as some previous studies also showed.

Mainstream yields of nicotine and nicotine-free dry condensate are not significantly affected by this barometric pressure change, except for sample AB - probably due to a lack of uniformity. That means the per puff yields are lower for high-altitude smoking; in other words, mainstream smoke becomes smoother.

Mainstream gas-phase yields do not show significant differences except again in the AB sample. The CO and CO2 formation processes during the cigarette smoking are not very noticeably affected, as a whole, by barometric pressure within the studied range.

TABLE 3 : Puff-count and mainstream results

Sample	Location	Puff-count	Nicotine [mg/cig]	PMWNF [mg/cig]	CO [mg/cig]	CO2 [mg/cig]
AB	Sevilla	9.0	1.11	16.1	17	52
	Madrid (3.0)	9.2*	1.16**	16.8*	16	47**
	Madrid (3.5)	9.2*	1.12	16.6	16	49**
DAC	Sevilla	7.7	0.56	11.5	14	42
	Madrid (3.0)	8.1***	0.57	11.4	14	42
	Madrid (3.5)	8.1***	0.55	11.3	14	42
1R4F	Sevilla	9.1	0.94	11.6	12	43
	Madrid (3.0)	9.5***	0.96	11.6	12	41
	Madrid (3.5)	9.5***	0.95	11.5	12	43

* significant at 90 %; ** significant at 95 %; *** significant at 99 %

The summary of the sidestream results appears in Table 4.

The results of sidestream nicotine show significant differences when comparing Sevilla and Madrid yields at 3.0 litre per minute. The figures for nicotine are arrived at by adding nicotine collected on the sidestream Cambridge filter to nicotine deposited on chimney walls. On average, the difference observed is a 7 % for a 8.6 % change in barometric pressure. However, the differences are not significant when comparing Sevilla Madrid-3.5 litre per minute results.

Sidestream nicotine-free dry condensate yields are arrived at by adding condensate collected on the sidestream Cambridge filter to the estimation of that deposited on the chimney walls condensate. The results show again a significant difference of a 7 % on average between Sevilla and Madrid yields at 3.0 litre per minute. The results obtained in Madrid at 3.5

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Added sugars altered the combustion characteristics of cigarette (Table 1); they burn faster and have their maximum of weight loss in the temperature zone 350-500°C which is by some authors characteristic for phenol synthesis.

Table 1 :

Weight loss as determined by TGA.

a - temperatures of weight losses
b - % of weight loss

Vzorek / Teplota	A		B		C		D		E	
	a	b	a	b	a	b	a	b	a	b
100			60 90	2 9	81,5	4				
200	150	9	110 120 137	11 15 23,2	138	8	110 200	49% 58%	119	23,6
300	258	16,4	201 250	38,5 46,2	287	22,8	280	72,2	212 299	52 68,3
400	322 378 390	27,5 42,5 45,1	370	61,3	318	31,1			357	74,5
500	440	51					420	87,4	426,8	78
600			550	82,5	506	60,08	524	98,2	536	96
650	630	80%			639,8	80				

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Single-residue and multiresidue methods for the determination of pyrethroid insecticides have been reported (1-8). These compounds are easily analyzed by gas-liquid chromatography because of their thermal stability and electron capturing properties. However the non specific nature of ECD introduces the further requirement that a methodology be developed to provide interference-free extracts.

To this end in the present method Solid Phase Extraction was used for clean-up step. Solid Phase Extraction (SPE) is a rapid and efficient sample preparation technique based on separation mechanisms of liquid chromatography. SPE tubes are prepared by suppliers in the same manner as corresponding packings in HPLC columns. This packings ensure highly reproducible extractions and a sample recovery usually greater than 95% and often very close to 100%.

The present method was tested for simultaneous determination of residues in tobacco of the following eight synthetic pyrethroids and their isomers: Tetramethrin, Permethrin, Cyfluthrin, Cypermethrin, Alfamethrin, Flucythrinate, Fluvalinate and Deltamethrin.

EXPERIMENTAL

-Apparatus and Reagents.

A gas-chromatograph Carlo Erba Series Mega mod.5300 equipped with a split-splitless or a cold split-splitless injector, a temperature programmer and a ^{63}Ni electron-capture detector(ECD) was used. The ECD was operated at a temperature of 300 °C in the constant period mode with a pulse width of 1 μsec. The chromatographic column was a 25 m x 0.32 mm i.d. capillary column with an OV-1 stationary phase of film thickness 0.10-0.15 μm. The carrier gas was helium with a flow rate of 0.5 ml/min. Additional make-up gas (nitrogen) was added to the capillary effluent at a flow rate of 50 ml/min.

The gas-chromatographic conditions were the following:

a) Split-splitless injection system

Injector temperature = 250 °C

Oven temparature = isothermal at 215 °C for 18 min followed by temperature programming to 220 °C at 5 °C/min, isothermal at 220 °C for 18 min and temperature programming to 250 °C at 10 °C/min. The final temperature was mantained for 8 min.

The split ratio was 1:10.

b) Cold split-splitless system

Injector temperature = initial 60 °C, final 250 °C

Splitless time = 10 sec. Purge time = 1 sec.

The other chromatographic conditions were as above.

In all cases the chromatograms were recorded by using a HP3699 computing recorder.

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litre per minute are not significantly different from the Sevilla yields except for sample DAC.

Sidestream gas phase results do not reveal so significant differences either for CO or CO2 yields, except for sample AB, between Madrid and Sevilla smoking. Values of CO and CO2 by volume are certainly different, but the differences are lower when the results are expressed in weight units, taking into account the actual barometric pressure.

TABLE 4 : Sidestream results

Sample	Location	Nicotine [mg/cig]	PMWNF [mg/cig]	CO [mg/cig]	CO2 [mg/cig]
AB	Sevilla	4.90	33.0	62	506
	Madrid (3.0)	5.22***	34.6***	66**	504
	Madrid (3.5)	4.97	32.4	66**	518
DAC	Sevilla	2.24	26.4	57	406
	Madrid (3.0)	2.48***	29.2***	60*	419
	Madrid (3.5)	2.31	28.1**	60*	423*
1R4F	Sevilla	5.63	34.3	61	473
	Madrid (3.0)	5.98***	36.1***	60	478
	Madrid (3.5)	5.76	34.2	64**	491*

* significant at 90 %; ** significant at 95 %; *** significant at 99 %

As a summary, the most significant results were hence: (1) barometric pressure affects puff-count - i.e. cigarette burning - slightly but significantly; the lower the barometric pressure the slower the cigarette burning; and (2) an increase of 7 % in sidestream nicotine and PMWNF could be measured when barometric pressure decreased by 8.6 % and this variation could be "corrected" increasing the flow rate in the chimneys up to 3.5 litre per minute.

Obviously, the amount of oxygen available is lower at low barometric pressure and, consequently, the burning conditions of the cigarettes could be equivalent to a lower flow rate in the chimney. So, the increase of flow rate from 3.0 to 3.5 litre per minute in the chimney in order to "correct" the yield figures could be a practical way to compensate for the effect of lower oxygen available at low barometric pressure.

However, a closer examination of the results suggests other interpretation. The lower flow rate in the chimney could certainly affect the burning characteristics - as the puff-count observed-differences reveal - and condensation and coagulation of sidestream-smoke particles in such a way that an increase of sidestream-smoke yields is to be found (3,4). But, if the formation mechanisms of smoke particles could be affected by flow rate, the efficiency of the sidestream Cambridge filter could also be affected, as a consequence. All the main observations of this experiment on sidestream condensate, even the "corrected-by-flow" test, could be explained by a loss of efficiency in the sidestream Cambridge filter owing to modified flow and size distribution of sidestream-smoke particles. On the other hand, gas phase results show

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DETERMINATION OF RESIDUES OF EIGHT SYNTHETIC PYRETHROIDS IN TOBACCO BY CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A method was developed for the simultaneous determination of the residues of the following eight synthetic pyrethroids and their isomers in tobacco: Tetramethrin, Permethrin, Cyfluthrin, Cypermethrin, Alfamethrin, Flucythrinate, Fluvalinate and Deltamethrin. The pesticides were extracted from ground tobacco with acetone:water 9:1 for 5 hours. The extract was diluted with water and partitioned into n-hexane. The organic phase was concentrated to about 1 ml and then purified by a Florisil-SPE column. The elution was carried out according to the following pattern:
1) fraction 1 = hexane (3 ml)
2) fractions from 2 to 8 = hexane:diethylether 9:1 (2 ml each)
3) fraction 9 = diethylether (20 ml).
Tetramethrin was found in fraction 9. The other pyrethroids in the fractions from 4 to 8.
The gas-chromatographic analyses were run with a gas-chromatograph Carlo Erba Series Mega HRGC 5300 equipped with a capillary column (stationary phase OV-1 - 0.10-0.15 µm film thickness, 25 m long) and a ^{63}Ni electron capture detector. Two different injection ports were used: split-splitless and cold split-splitless, working both with isothermal and programmed temperatures. The latter shows chromatograms with lower drift and lower noise, while the former gives a higher sensitivity. Both the limit of detection and the limit of determination were estimated for each compound. Recoveries from fortified samples at level of 1 ppm are reported.

INTRODUCTION

The pyrethroid insecticides are the object of intense interest for use in tobacco protection because of their desirable environmental properties of short persistence and nontoxicity to mammals. These features, combined with their broad spectrum of insecticidal activity and with their toxicological properties which permit the control of certain insects at very low application rates, have made the pyrethroids environmentally safe and acceptable alternatives to the older organochlorine compounds and to the natural pyrethrins. The rapid increase in their application and the recent commercial introduction of some new pyrethroids compounds require a method by which the residues of as many pyretrhroids as possible can be determined.

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RESULTS AND DISCUSSION

Figures 1 and 2 show typical chromatograms obtained by injecting 1 µl of mixed standard pyrethroids solution (1 µg/ml each) into gas-chromatograph equipped respectively with split-splitless and cold split-splitless injection port. The numbers of the peaks in both figures correspond to the compounds listed in table 2. It is clear that the latter system shows chromatograms with lower drift and lower noise, while the former gives a higher sensitivity for some compounds.

TABLE 2
GAS-CHROMATOGRAPHIC PEAKS OF SYNTHETIC PYRETHROIDS

Pyrethroids	Peak Numbers
Tetramethrin	1-2
Permethrin	3-4
Cyfluthrin	5-6-7-8
Cypermethrin	9-10-11-12
Alfamethrin	11
Flucythrinate	12-13
Fluvalinate	14-15
Deltamethrin	16

While the stereo-isomers of each pyrethroid are resolved by the capillary column used, it was unable to separete a Cypermethrin isomer from one of Flucythrinate. However these compounds can be easily determined as they are present in different fractions of SPE tube eluate.

As shown in figure 3, no coextractant from untreated tobacco interferes with the pyrethroids tested.

All synthetic pyrethroids examined were quantitatively analyzed under GLC conditions given above by determining the sum of their isomers. Detector responses were linear in the range 0.01-1 µg/ml. For each compound the calibration curve, based on peak area measurement, was a straight line and passed through the origin. The correlation coefficients were in the range 0.9989-0.9999.

Table 3 shows the limits of detection and the limits of determination, estimated for each pyrethroid according to OFC Pesticide Commission Method (9).

The recovery at 1 ppm level was checked by adding known volumes of a mixed pyrethroid standard solution in hexane to five suitable portions of tobacco shown not to contain residues of the pyrethroids. The samples were then treated as described in "Procedure". The results obtained are reported in table 4.

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